Renewable and Sustainable Energy Reviews 16 (2012) 6455–6475

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Medium-temperature conversion of biomass and wastes into liquid products, a review

Eugenia Sannita, Bahar Aliakbarian, Alessandro A. Casazza, Patrizia Perego, Guido Busca*

Dipartimento di Ingegneria Civile, Chimica e Ambientale, Università di Genova, p.le J.F. Kennedy, I-16129 Genova, Italy

A R T I C L E I N F O

Article history:
Received 19 October 2011
Received in revised form
5 June 2012
Accepted 8 June 2012
Available online 3 September 2012

Keywords:
Biomass pyrolysis
Catalytic conversion
Plastics pyrolysis
Waste pyrolysis
Vegetal oils
Rubber pyrolysis
Biofuels

A B S T R A C T

The subject of this review is the production of new-generation biofuels and fuels from wastes by cost effective medium temperature conversion processes. Recent literature results concerning pyrolysis at medium-temperature (mainly 300–450 °C) of biomasses, plastics and wastes are reviewed. The focus is on processes usable to maximize the production of liquids. Conclusions concern the relation of raw material composition and reaction temperature on the quality and quantity of liquid products. The main limitation of this approach is the high heteroatom content that is frequently present in the resulting fuels, particularly oxygen from biomass-derived fuels, but also nitrogen, sulphur and chlorine from waste derived fuels. For this reason, further refining treatment could be necessary, depending on the use of the resulting fuel.

Contents

* Corresponding author. Tel.: +39 01 0353 6024.
E-mail address: Guido.Busca@unige.it (G. Busca).

1364-0321/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.rser.2012.06.017

1. Introduction

Considerable efforts have recently been devoted to substituting raw fossil materials with renewable sources for the production of energy. The primary motivation for these efforts is associated with the need to reduce the emission of greenhouse gases to avoid further contributions to global warming. In this respect, biofuels may be required to fuel cars and trucks and to produce electrical energy or heat.

Bioethanol produced by amidaceous raw materials and biodiesel, which is fatty acid methyl esters produced by the transesterification of vegetable oils, are usually considered to be first generation biofuels, for which there are well established production processes. However, the production and use of these biofuels results in several drawbacks. Both production processes are actually not optimal from energetic and environmental points of view. The use of first generation biofuels in car engines is currently limited by notable costs and their oxygen content, which is primarily to avoid pollution by aldehydes in the waste gases. Other problems concerning first generation biofuels are the sustainability of their production in energetic terms and their competition with the food industry.

Several different types of treatments (Fig. 1) are being considered to produce second generation biofuels to overcome these drawbacks [1,2]. The majority of research interest is devoted to developing gasification technologies followed by syngas purification and Fischer–Tropsch syntheses [3,4]; however, the efficiency of this process is estimated to be quite low [5]. Hydrothermal treatments may allow the production of liquids that are primarily formed by highly oxygenated small monomeric molecules, which require further conversion to fuels and is energy intensive [6]. Simple thermal treatments, with or without catalysts, are also being considered to produce fuel gases, gasolines or bio-oils that are applicable as fuels. Similar thermal processes could also be applied to several different types of residues, such as plastic wastes, to recover energy and reduce waste material [7–9]. High temperature processes may allow the production of gasolines and gases that are potentially applicable as fuels. In the present work, we will specifically focus our interest on treatments performed in the temperature range of 300–450 °C. The processes realized in this temperature interval could be useful for producing liquid mixtures that could be used to obtain fuels. These pyrolysis processes may be cost-effective compared to alternative processes.

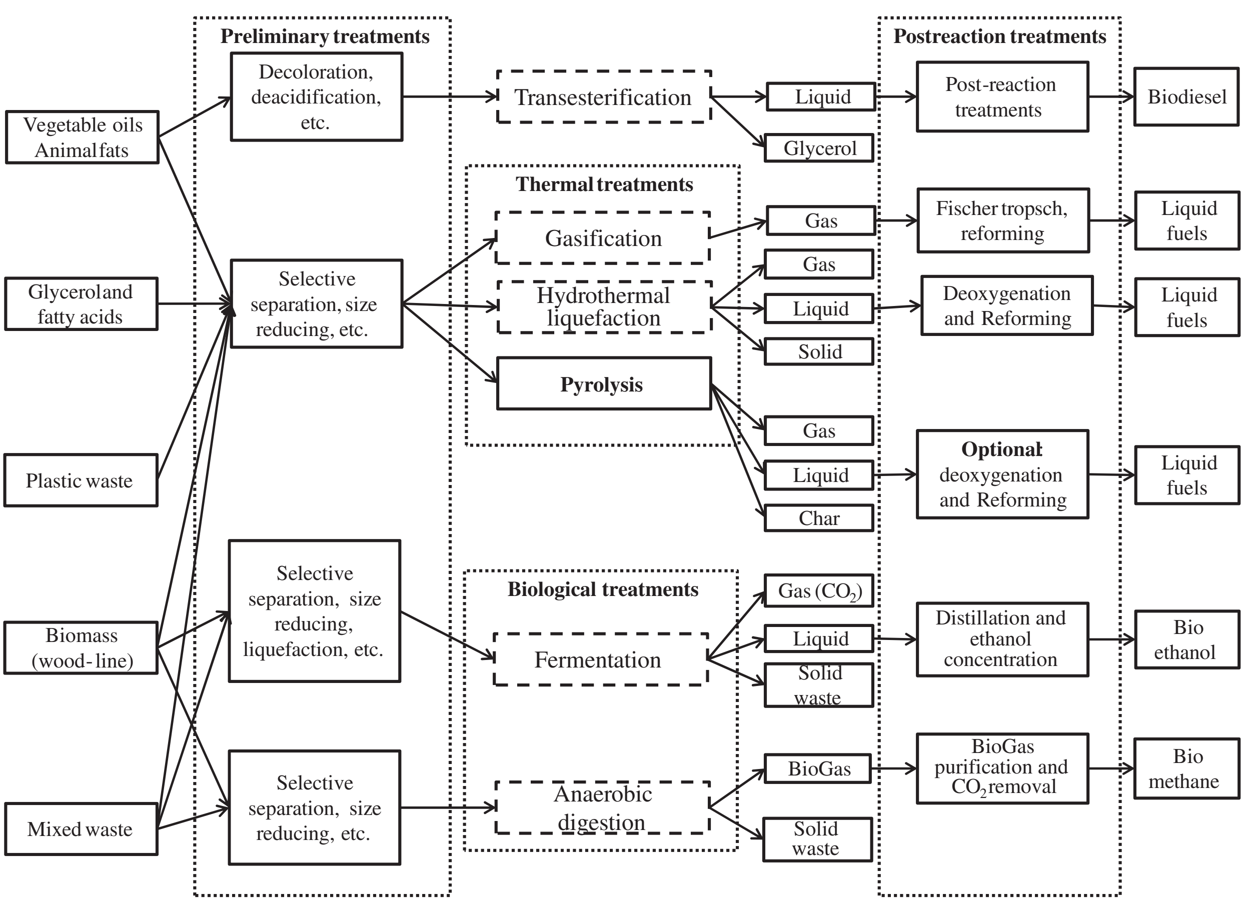


Fig. 1. Biomass upgrading by chemical, thermal and biological treatments.

Table 1
Composition of materials based on triglycerides.

Oil or fat	C6	C8	C10	C12	C14	C16	C16:1	C18	C18:1	C18:2	C:18.3	C20	C20:1	C20:5	C22:0	C22:1	C22:6	C24:0
Soybean					< 0.5	7.0–11.0		2.0–6.0	19.0–34.	43.0–56.0	5.0–11.0	< 1.0						
Sunflower					< 1.0	3.0–6.0		1.0–3.0	14.0–35.0	44.0–75.0	< 1.5	0.6–4.0			0.8			
Rapeseed						4.9		1.6	33.0	20.4	7.4					23		
Palm oil					0.5–2.0	32.0–45.0		2.0–7.0	38.0–52.0	5.0–11.0								
Peanut oil						6.0–9.0		3.0–6.0	52.0–60.0	13.0–27.0		2.0–4.0			1-3			1-3
Olive oil					0.1–1.2	7.0–16.0		1.0–3.0	65.0–80.0		4.0–10.0	0.1–1.3						
Coconut	0–0.8	5–9	6.0–10.0	44.0–52.0	13.0–19.0	8.0–11.0	2.5	1.0–3.0	5.0–8.0		0–1.0	0–0.5						
Cottonseed					0.4	20		2	35	42	0.1–2.1	< 0.5						
Jatropha					0.5–1.4	12.0–17.0		5.0–9.5	37–63	19–41		0.3						
Tallow					3–6	24–32		20–25	37–43	2–3								
Lard					1–2	28–30		12–18	40–50	7–13	0–1							
Yellow Grease					1.3	17.4		12.4	54.7	8.0	0.7	0.3						
Chicken fat						20.0	6.2	5.3	39.6	24.7	1.3							
Fish oil					6.0	15.9	4.4	3.1	17.3	21.0			7.6	5.1		10.4	4.5	
Swine lard					1.4	24.1	2.4	14.0	39.4	14.2	0.8		0.7					
Beef tallow					2.9	28.7		19.5	44.4	3.6	0.9							

2. Conversion of triglyceride- based materials

Both vegetable oils and animal fats are primarily composed of triglycerides [10]. These materials are considered to be a promising family of raw materials for the production of renewable fuels using thermal processes [11–17]. Table 1 summarizes some properties of materials that belong to these families. As can be observed from these data, the oils differ significantly based on the distribution of the fatty acids that form the triglycerides. According to Demirbas [15], the primary vegetable oils are from coconut (copra), corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut (groundnut), safflower, sesame, soybean, and sunflower. For example, soybean and sunflower oils have a particularly high linoleic acid content (C_{18} with a double unsaturation) and are primarily composed of C_{18} fatty acids (stearic, oleic, linoleic and linolenic), whereas in palm oil, palmitic acid (C_{16} saturated) and oleic acid (C_{18} monounsaturated) are significantly present. Animal fats are normally composed of triglycerides with a saturated acid content that is higher than that of vegetable oils.

2.1. Thermal treatment of vegetable oils

The results available from a literature review on the thermal conversion of vegetable oils were summarized by Maher and Blessler in 2007 [13] and by Demirbas in 2009 [15]. The studies in this field are typically performed in batch reactors and more rarely in fluxed tubular reactors in the temperature range of 300–500 °C. Different types of vegetable oils have been studied, including tonga oil [18], sunflower oil, soybean and saffron oils [19], rapeseed oil or canola oil [20], soybean, palm and castor oils [21], macauba fruit oil [22,23], different tropical fruits oils, such as piqui, babbassu and palm oils [24] and cottonseed oil [25].

Note that the results reported by Schwab et al. [19] in the latter half of the 1980s are among the most significant and complete studies. These authors characterized a product that was pyrolyzed/distilled from soybean oil, which was composed of 31.3% alkanes, 28.3% alkenes, 2.4% aromatic hydrocarbons, 9.4% diolefins, 12.2% carboxylic acids with C_4–C_{20} chains, over 10.9% unidentified compounds, and it had a cetane number of 43 with yields greater than 70%.

The majority of the subsequent studies have been focused on the use of soybean oil. Using a thermogravimetric system, Ngo et al. [26] observed that the decomposition of soybean oil begins at approximately 300 °C and is completed at temperatures below 500 °C.

Prado and Filho [27] reported that the thermal conversion of soybean oil occurs at 380–400 °C. After 150 min, the conversion reached 93%, with a 77% yield of a heavy liquid product that was characterized by a boiling point greater than 270 °C and primarily composed of hydrocarbons (alkanes, alkenes and aromatics), alcohols, ketones and carboxylic acids (C_6–C_{30}). In this fraction, 6% was composed of a light organic fraction (C_4–C_{14}), 7% of a solid defined coke, 9% of a gas and 1% of an aqueous fraction.

According to Luo et al. [28], who used a dynamic system at a heating rate of 2 °C/min and a residence time of 30 min, operating at the reduced pressure of 3 kPa, the degradation reaction of soybean oil begins at 370 °C. At 430 °C and after 10 min, the yield in a light fraction (Tb < 300 °C) is 34%. This fraction is composed of 28% alkanes, 1.1% aromatics, 1.1% olefins and 34% fatty acids. When rapeseed oil is used, a higher yield in the light fraction is achievable (46%); furthermore, this fraction is richer in acids (41%).

E-mail address: Guido.Busca@unige.it (G. Busca).

Junming et al. [29] studied the decomposition of soybean oil in a reactor/distiller at 340 °C and obtained a yield greater than 70% in the diesel fraction, which was characterized by scant cold properties due to the considerable presence of acids, as highlighted by an acid value (AV) of 111 mg_{KOH}/g.

In the second half of the 1990s, the N.N. Bakhshi group of the Saskatchewan University (Canada) accomplished considerable work on the conversion (thermal and catalytic) of canola oil using a fluxed tubular reactor. These authors [20,30] demonstrated that canola oil already converts at 300 °C, and it primarily produces a liquid fraction at low temperatures. At temperatures greater than 400 °C, the conversion is completed, but the primary product is gaseous. These authors highlighted the effects of spatial velocity (SV) and temperature (300–500 °C) on the conversion of rapeseed oil. When the spatial velocity decreases, the temperature increases, which results in the conversion of the product from a liquid to a gas. At 370 °C, the formation of aromatic hydrocarbons begins. These authors also studied the effect of adding water vapor on the thermal pyrolysis; water vapor moderately inhibits the conversion and causes the shift of the main products to compounds with a higher number of carbon atoms.

In the second half of the 1990s, a group from the Istanbul University [31] studied the thermal and catalytic pyrolysis of exhausted sunflower oil in a static reactor/distiller. In the thermal process, the conversion was 43% at 400 °C, and it increased to 55% at 420 °C. These authors washed the product with 0.5 M methanolic potassium hydroxide, thereby separating an acid phase from an organic liquid without carboxylic acids. At 400 °C, the authors reported yields of 14% of a gaseous phase, 20% of an organic phase and 4.2% of an acid phase. At 420 °C, these yields increased to 21.6%, 23.9% and 4.5%.

Concerning palm oil, Lima et al. [21] reported pyrolysis data at 330–380 °C; this process produced 7% of products that were characterized by a boiling point of Tb < 80 °C, 9% with a Tb in the range of 80–140 °C, 9% with a Tb between 140 and 200 °C and 75% with a Tb > 200 °C. This last fraction has a density of 818 kg/m^3 at 20 °C, a viscosity of 2.7 cSt at 40 °C, an acid value of 133 mg_{KOH}/g and a cetane number of 52.7, which satisfy the Brazilian specifications for biofuels.

Twaiq et al. [32] studied the thermal conversion of palm oil at 450 °C in a dynamic system. In the operative conditions of this study, the conversion was 38.5% with a yield of 15.2% in a diesel fraction, 12.1% in gasoline, 6.5% in kerosene and 4.7% in gas.

One of the most relevant parameters in the conversion of oil is the actual reaction time (or permanence time in the reactor), which is also related to the reactor type. For example, Onay and Kockar [33] studied the pyrolysis of rapeseed oil in a "free fall" reactor that allows short residence times with only partial conversions, even at very high temperatures (maximum conversion of 87.8% at 700 °C, maximum yield in a liquid product of 72–75% at 600 °C). These authors characterized the reaction products using IR spectroscopy and elemental analysis. They measured an oxygen content of 13–15% wt/wt in their liquid products and a nitrogen content of 3–6%. This result appears to be significant because no other authors have reported the presence of nitrogenous products. Furthermore, these authors concluded that further treatments are required to use the obtained products as diesel-like fuels.

With continuous reactors, very low permanence times are used and low conversions and yields are obtained. In contrast, with batch reactors or discontinuous reactor/distillers, the reaction times and the yields are higher. The data reported in the literature substantially agree with the results reported by Onay and Kockar, which indicated that vegetable oils (based on triglycerides) decompose in the range of 300–450 °C to yield a hydrocarbon mixture (alkanes and alkenes with a minimum amount of aromatics) and oxygenated compounds, including alcohols, carbonylic compounds and carboxylic acids.

With increasing temperature and reaction time, the conversion reaction can be completed, and the liquid yield tends to decrease, thereby producing larger amounts of gases; however, the amount of organic fraction (in terms of carbon atoms number) decreases, which produces a greater amount of volatile molecules (gasoline), to the detriment of those fractions that are less volatile (diesel).

Different authors [11,18,20,24] agree that the decomposition process of triglycerides involves two different and subsequent steps.

In the first step, which is called primary cracking, the C–O bonds are supposed to break, and the glycerol chain is supposed to undergo a cracking reaction. This stage appears to produce free fatty acids. In the second stage, which is called secondary cracking, free fatty acids are supposed to decompose to form hydrocarbons.

The presence of oxygenated compounds, specifically carboxylic acids, is directly associated with the poor cold flow properties (high freezing point and cold filter plugging point) of these oils and with the possible consequences of their corrosive potential, which can be limited by further treatments.

According to Lima and coworkers [21], if the proper operative distillation conditions are chosen, the pyrolysis products of soybean, palm and castor oil (at 330–400 °C) can satisfy the Brazilian specifications for their use as biofuel.

Furthermore, after the thermal stage, these authors suggest the use of a second catalytic stage to decompose the carboxylic acids that are present, which improves the properties of the product.

Doll et al. [34] measured the density, viscosity and surface tension of a refined soybean oil pyrolysis product (at 350 °C), and they obtained values that were comparable to those of petrochemical diesel fuels. These authors also studied the oil produced from the pyrolysis of soybean oil derived soap (in the same operative conditions), and they obtained similar results.

The pyrolysis of vegetable oils has also been occasionally studied at higher temperatures. Wiggers et al. [35] studied the conversion of soybean oil during a "fast pyrolysis" process using a tubular pyrolizer while adding different amounts of water. According to these authors, the best result was obtained at 525 °C with a reaction time of 25 s without water, which produced a bio-oil characterized by a calorific value of approximately 42 kJ/kg and a yield of 72%.

In agreement with Songthanapitak et al. [36], the reaction (6 hours) of palm oil at 600 °C produces a diesel fuel, whose properties (pour point of 0.77 °C, 0.012% of ash, specific gravity of 0.834, viscosity of 3.57 cSt at 40 °C and 2.98 cSt at 50 °C, flash point of 18.5 °C, color value of 2.5–3.5, and calorific value of 43,937 kJ/kg) allow the products to be within the specifications of a diesel fuel, with the only exception of the color value. However, the authors did not report the yields of the product.

2.2. Catalytic conversion of vegetable oils

2.2.1. "catalytic cracking" of vegetable oils

The term "catalytic cracking" is generally used to indicate a process that is similar to the refining process performed with vacuum gasoils and deasphalted oils, which is denoted as Fluid Catalytic Cracking (FCC). In practice, solid acid catalysts, fluidized and entrained bed systems with catalyst regeneration and recycle (as it happens in the FCC process) and fixed bed reactors are used. The operative range for the temperature is 400–600 °C; consequently, the feed is essentially in the vapor phase [37].

The possibility to convert vegetable oils into hydrocarbons using processes such as the ones described above was initially proposed by the Mobil research group [38] shortly after the discovery of the particular properties of the zeolite H-ZSM-5, which they developed during a study on "shape selectivity".

Table 2
Summary of the catalysts used in high-temperature pyrolysis of vegetable oil and animal fats.

Catalyst description.	References
Microporous silica	[30]
Mesoporous silica	[37]
Silicalite	[30]
Microporous amorphous silica alumina	[165]
Mesoporous Al-MCM41 type (pores in hexagonal phase)	[26,32,166]
Al-SBA-15 type (disordered pores)	[167,168]
Acid zeolites of H-ZSM-5 (H-MFI) type (medium pore size)	[26,169,170]
H-beta (HBEA)	[167,169]
H-mordenite (H-MOR)	[165]
Acid zeolites of Faujasite HY (H-FAU) type (large pore size)	[165]
Ultra stable HY (H-USY)	[169]
Rare Earth Y (REY)	[171,172]
Aluminum-pillared clay (AL-PILC)	[165]
Zeolite-silica alumina composite catalysts with micro structure	[173]
Zeolite-silica alumina composite catalysts with mesoporous structure	[167,170]
FCC commercial catalysts (usually based on mixture of REY and H-ZSM-5 zeolites with kaolin and silica alumina)	[25,174]
Model mixtures of zeolites	[171]
Composite catalysts containing acid phases and metallic catalysts	[175]

The catalysts used in literature reports, as mentioned previously, are usually solid acids. The catalysts employed by different authors are reported in Table 2.

The typical temperature range used in these studies is between 450 °C and 600 °C, which is lower than that used in the FCC processes. The reaction is performed under atmospheric (or slightly higher) pressure. Generally, the goal is to produce gasoline with a high octane number and/or fuel gases. According to Twaiq et al. [170], the optimal conditions to produce gasoline is to mix a medium pore zeolite with a mesoporous silica alumina, which produces the optimum catalyst. For cottonseed oil, an optimum temperature of 426.2 °C is reported, with a residence time of 50.2 s and a yield of 65.6% in light diesel [25]. With REY zeolites (Zeolite Y with rare earths), the optimal operative conditions to produce a gasoline rich in aromatics are 450 °C, residence time of 20 s, catalysts/oil ratio of 5 g/g [37]. According to Melero et al. [174], the catalytic cracking of different vegetable oils (palm oil, soybean oil and cooking-waste oil) on a commercial FCC catalyst at 565 °C produces a fraction without oxygenated compounds because all of the oxygen is removed in the form of CO, CO_2 and H_2O. Nevertheless, the product contains a significant amount of aromatics.

2.2.2. *Catalytic conversion of vegetable oils at moderate temperature*

In the present work, the conversion of vegetable oils at temperatures lower than 450 °C is defined as catalytic pyrolysis. Lower temperatures may be optimal for the production of diesel-like fuels.

In 1983, Dos Anjos et al. [39] studied the decomposition of natural and pre-hydrogenated forms of soybean oil, beginning at 300 °C on alumina and magnesium oxide catalysts. These authors observed considerable activity of both catalysts at 300 °C and a remarkable effect of the pre-hydrogenation that could result in the production of a mixture rich in hydrocarbons as the catalytic pyrolysis product. Furthermore, they reported that, when using magnesium oxide, a remarkable amount of aromatics was obtained, which is contrary to what is observed when using alumina.

The study by Weisz et al. [38], a research group that worked for Mobil, is among the first works that used acid zeolites for converting vegetable oils into biofuels and is a classic example of a catalytic conversion study. In particular, these authors demonstrated the possibility of producing gasoline fractions rich in aromatics using a zeolite they developed (H-ZSM-5).

Nevertheless, it has been reported that jojoba oil could be completely converted at 400 °C on the zeolite, whereas to convert corn and castor oils, higher temperatures (500 °C) were necessary.

Jiunming et al. [29] used an alumina and mesoporous silica (type MCM41) catalyst at 340 °C in a reactor/distiller to obtain diesel in yields of 71–74%, which were slightly higher than those obtained without the use of a catalyst. Furthermore, these products have a slightly lower acid value (104–107 mg_{KOH}/g). Idem et al. [21] compared the catalytic activity of different acid and basic catalysts during the conversion of rapeseed oil at 400 °C. First, they observed that the presence of catalysts slightly modifies the conversion and yield for different products, even in the case of the thermal process. According to these authors, at 400 °C with mild acid catalysts, such as silica and alumina, the conversion is higher than that obtained using a catalyst with stronger acid properties, such as silica-alumina and the zeolite H-ZSM-5. At 400 °C, the highest yield of organic product is obtained through the use of amorphous silica, silicalite (microporous zeolitic silica) and silica-alumina. The majority of acid catalysts can cause an increase in the content of aromatic hydrocarbons, whereas using alumina and silica-alumina catalysts can apparently decrease the content of oxygenated compounds. Nevertheless, these authors observed the presence of significant amounts of unidentified products (up to 30%).

Dandik and Aksoy [40] compared the effects of the zeolite H-ZSM-5 and amorphous silica-alumina catalysts on the conversion of exhausted sunflower oil at 400 and 420 °C. The conversion appeared to be quite similar in both cases, but the zeolite produces a larger amount of gases and a smaller amount of acids, whereas the silica-alumina produces a greater amount of organic liquid.

Similarly, Katikaneni et al. [165,173] compared the effects of the zeolite HZSM-5 and amorphous silica-alumina catalysts on the conversion of rapeseed oil at 400 °C. The conversion appeared to be similar with the use of both catalysts, but the zeolite produced more gases and a greater liquid fraction (with more aromatics) with considerably less coke. For both catalysts, the increase of the spatial velocity clearly results in a reduction of the conversion and of the production of gaseous products. However, the effect of the spatial velocity on the production of the liquid fraction and coke fraction is opposite for both catalysts; at higher SV values, the coke fraction decreases whereas the liquid fraction increases when silica-alumina was used, as expected. In contrast,

the opposite behavior occurs with the use of the zeolite. These authors also examined the effects of water vapor. At 400 °C, the conversion decreases in the presence of water vapor at low SV; nevertheless, it increases slightly at high SV. However, it appears that the primary effect of water vapor is to decrease the production and this reduction in coke content results in a lower deactivation of the catalyst.

Prado and Filho [27] used bauxite (aluminum and iron oxides and hydroxides) as a catalyst for the pyrolysis of soybean oil at 380–400 °C. These authors concluded that the catalyst slightly modifies the conversion and the yield of the products for the simple thermal reaction. In both cases, the largely predominant product is a relatively heavy organic liquid (yield of 70%). Nevertheless, the amount of carboxylic acids in the product is decreased in the presence of the catalyst, and the acid value is reduced to 84 mg_{KOH}/g.

According to the data reported by Twaiq et al. [169], at 350 °C and with a WHSV of 1 1/h, the zeolite H-ZSM-5 is more active in the conversion of palm oil than the zeolites with higher pore dimensions, such as zeolite H-beta and H-USY (ultrastable Y faujasite). Zeolite H-ZSM-5 also produces a greater gasoline and gaseous yield, whereas zeolites H-beta and H-USY provide a higher selectivity for diesel products, even though the conversion of the oil is incomplete. This behavior can be attributed to the smaller tendency of the zeolite H-ZSM-5 to deactivate coking. The pores of this type of zeolite (approximately 5.5 Å in diameter) do not allow the internal formation of aromatic rings, in contrast to the zeolites with larger pores. This behavior might occur because the pores of the zeolite H-ZSM-5 are sufficiently large to allow the penetration of the reactants in addition to the intermediate compounds. However, the characterization of the products in this study is extremely limited. Only the data on the presence of aromatic hydrocarbons in gasoline are reported. Values of aromatic fractions up to 10% suggest that part of the reaction occurs outside of the zeolitic cavities. However, data on the presence of oxygenated compounds are not reported.

These authors also reported that the addition of potassium to the zeolite H-ZSM-5 causes its deactivation; this result demonstrates the acid catalysis nature of the reaction on this zeolite.

Similarly, Siregar and Amin [41] reported that the exchange with copper decreases the activity of the zeolite HZSM-5 at 500 °C, which shifts the product yields towards heavy residuals and coke.

The specific activity of the zeolite H-ZSM-5 to produce aromatic hydrocarbons (benzene, toluene, xylene, and BTX) during the conversion of rapeseed oil, with yields of 36% at 375 °C, have already been reported by Katikaneni et al. [165]. The experiments were performed in a continuous fixed bed microreactor that was made of stainless steel (length of 40 cm; internal diameter of 1.15 cm) and occurred inside of a coaxial cylindrical oven at 375–500 °C with a WHSV of 1.8 1/h. The maximum conversion was 100% at 450 °C, whereas the maximum yield in liquid products was 70% at 400 °C, with a large predominance of aromatic hydrocarbons. The maximum yield in gaseous products was 50% at 500 °C.

The gases are rich in light hydrocarbons (propane and butane), especially at high temperatures. The amount of BTX obtained with zeolite HZSM-5 is greater than that obtained using silica-alumina and aluminum-pillared clays, and also with other zeolites, including H-mordenite and H-Y.

The production of aromatics is also very high when using silicalite. This is quite surprising because this catalyst is the purely silicic and, thus, non-acidic, form of H-ZSM-5 zeolite.

This result would confirm the role of the dimensions of the pores during the production of aromatics. Aromatics tend to penetrate into larger pores, which poisons beta type zeolites, such as mordenite and faujasite. In the cases of the H-ZSM-5 zeolite, which has smaller pores, and the amorphous systems, the aromatics do not poison the catalyst and remain in the products.

Dandik et al. [40] concluded that by increasing the amount of catalyst (zeolite H-ZSM-5), the conversion of the used sunflower oil and the yield of the gaseous and liquid products increase to the detriment of the production of the acid phase.

Buzetki et al. [42] reported data on the conversion of rapeseed oil using zeolites in their sodium form (which are non-acid zeolites) as catalysts (zeolite Na Y and clinoptilolite). Using 2-10% by weight of the zeolite NaY and operating in the range of 350–440 °C with a residence time of 25–50 min, the authors reported a gaseous yield of 5–10% and a viscous residual with a yield of 5%. The main product is an oil that has comparable characteristics to those of a diesel fuel characterized by a bad smell, which is removable by distilling the light fraction with 6–10% at $T = 190$ °C. These authors reported that during the distillation, a portion of the light products react, which produced heavier products. The obtained products have a high acid value (110–130 mg_{KOH}/g). The GC–MS analysis revealed the presence of paraffins, olefins and carboxylic acids. The primary paraffinic product was heptadecane, whereas the predominant olefins were C_{17}. These products result from the decarboxylation of C_{18} acids (stearic, saturated, oleic, linoleic and linolenic, and unsaturated). In fact, rapeseed oil is primarily composed of triglycerides of C_{18} acids (95%). In contrast, when using sunflower oil, the primary product is pentadecane, which is the decarboxylation product of palmitic acid (saturated C_{16}).

The catalysts can be reused at least four times with similar results. Some authors reused the basic catalysts for the conversion of vegetable oils.

Idem et al. [20] examined the conversion of rapeseed oil at 400 °C on MgO and CaO catalysts. According to these authors, basic catalysts resulted in a lower conversion when compared to acid catalysts, and they produced a limited amount of gases and a high yield of liquid.

Dandik and Aksoy [43] converted sunflower oil in the presence of sodium carbonate at 420 °C. They reported a conversion of 82.7% with a liquid products (where the acids where removed by washing with potassium hydroxide) yield of 47.3%.

These authors also compared the results of using Na_2CO_3 with those of using acid catalysts (H-ZSM-5 and silica-alumina) and without the presence of catalysts (Dandik and Aksoy, [40]).

The authors reported a higher conversion of oil with the use of sodium carbonate. The use of sodium carbonate also resulted in a larger production of gases, a slightly higher hydrocarbon yield and a lower production of carboxylic acids.

According to Xu Junming et al. [44], the use of basic catalysts (potassium and sodium carbonates) during the conversion of soybean oil at 350–450 °C could result in the production of an oil that is almost free of carboxylic acids (with a yield of 73–75%), and thus, with optimal properties, such as a low freezing point and cold filter plugging point. Recently, the same authors [29] reported the conversion of soybean oil with basic catalysts at 300–340 °C. The authors used sodium, potassium and calcium carbonates and soda and calcium oxide as catalysts. They observed yields at a diesel fraction of 60–70% with acid values of 15–50 mg_{KOH}/g, which are quite low and thus satisfactory.

2.2.3. *Conversion of exhausted vegetable oils*

The composition of used frying oils is partially modified compared to the corresponding fresh oils, and the results obtained after the thermal treatment are identical to those obtained from treated fresh oils.

Data about the commercial fresh and used sunflower oils have been reported by Bezergianni [45]. In addition to the increase in density, an increase in the sulfur (most likely resulting from the food) and nitrogen contents (also derived from food or possibly

from the nitrogen present in the air) was observed. The results reported by Tamunaidu and Bhatia [171] are quite similar. In recent works [46,172], palm oil used in a restaurant was characterized after filtration (to remove solids) and compared to the fresh oil. The total concentration of unsaturated fatty acids increased in the used oil, whereas the palmitic and oleic acid contents decreased and the contents of palmitoleic, stearic and linoleic acid increased. It does not appear that the modifications resulting from the frying process substantially modified the properties of the oils in comparison to the pyrolysis processes.

In fact, Tamunaidu and Bhatia [171] and Bezergianni et al. [45] examined the conversion of fresh and waste vegetable oils. In all of the cited cases, the results indicate that adding waste oils to fresh oils during the pyrolysis process does not impart significant variations in the process itself. The only observed change was a slight difference in the amount and quality of liquid/gaseous products.

A group from the Istanbul University, Dandik and Aksoy [31,40,43], studied the thermal and catalytic pyrolysis of waste sunflower oil in a static reactor/distiller. During the thermal process, the conversion was 43% at 400 °C and reached values of 55% at 420 °C. These authors washed the liquid product with 0.5 M KOH to separate an organic liquid without carboxylic acids from the acid phase. Working at 400 °C, they reported yields of gaseous products of 14%, organic liquids of 20% and an acid phase of 4.2%. At 420 °C, these yields increased to 21.6%, 23.9% and 4.5%, respectively.

Dandik and Aksoy [31,40,43] have also compared the effects of the zeolite H-ZSM-5 and amorphous silico-alumina catalysts on the conversion of waste sunflower oil at 400 and 420 °C.

The conversion appeared to be quite similar in both cases; however, the use of the zeolites resulted in a higher production of gases and a lower production of acids, whereas silico-alumina resulted in a higher yield of organic liquid. The authors concluded that increasing the amount of catalyst (zeolite H-ZSM-5) during the oil conversion process increased the yields of the gaseous and liquid phases, whereas the production of the acid phase decreased.

According to Melero et al. [174], the catalytic cracking of different vegetable oils (palm oil, soybean and waste cooking oils) using a commercial FCC catalyst and working at 565 °C, produced a mixture without oxygenated compounds; all of the oxygen was removed as CO, CO_2 and H_2O. Nevertheless, the product contained several aromatic compounds as a result of the high processing temperature and the use of an acid catalyst.

These studies also provide evidence of rapid catalyst coking; therefore, continuous regeneration of the catalyst by coke burning was required, such as in the refinery FCC process. Table 3 summarizes the yields of the liquid products obtained from the medium-temperature conversion of vegetable oils.

2.2.4. Composition of the gases produced from the conversion of vegetable oils

Different authors have examined the composition of the gases produced by the thermal or catalytic cracking of the oils.

The primary components in the gases are light hydrocarbons [25], especially when working at high temperatures where the gaseous yield is high. The other products are CO and CO_2.

According to Idem et al. [20], the thermal decomposition of rapeseed oil produces a gas that is rich in ethylene (yield of 16.17% at 400 °C), propylene (3–10%), n-butane (2–5.5%), C_{5+} hydrocarbons (2.5–4.5%), CO and CO_2 (0.9–2.9%).

When working on alumina and silicoalumina, the $CO+CO_2$ yield significantly increases (4.2 and 5.5% at 400 °C). Katikanieni et al. [165] analyzed the cracking reaction of rapeseed oil with the zeolite H-ZSM-5 at 375 °C; the primary gaseous product was propane (10% yield) followed by C_4 hydrocarbons (butanes and butenes, 9.8%), C_5 (2.2%) and CO_2 (0.38%).

Only Prado and Filho [27] observed the presence of acrolein (pentenoic aldehydes, a compound with high toxicity) in the gas produced from the pyrolysis of soybean oil on bauxite. The amount of produced acrolein decreased when the quantity of catalyst was increased.

Acrolein is actually a dehydration product of glycerin, which is typically catalyzed by acid catalysts. Acrolein forms in considerable quantities along with other oxygenated compounds (especially acetaldehyde, hydroxyacetone, acetone, acetic acid and furane), and it also forms during the conversion of glycerin/water mixtures on acid catalysts [47]. Light hydrocarbons (mostly ethylene, propylene and butene) are also produced along with hydrogen, CO and CO_2 as primary products during the conversion of glycerin/water mixtures on acid catalysts.

Glycerin decomposes directly to $CO+CO_2+H_2$ in the presence of water on metallic catalysts at 300–450 °C [48]. These data clearly indicate that the origin of the gaseous molecules formed during the pyrolysis of vegetable oils at low temperatures is most likely due to the decomposition of the glycerol chain, whereas at

Table 3
Overview of liquid yield products from medium-temperature pyrolysis of different vegetable oils.

Vegetable oil	Reactor specification	Temperature (°C)	Catalyst	Liquid yield (%wt/wt)	Reference
Soybean oil	Batch-distiller reactor	–	(thermal cracking)	75	Schwab et al. [19]
Soybean oil	Fixed bed reactor	450	Ga/MCM41	77	Ngo et al. [26]
Soybean oil	Batch-distiller reactor	350–400	(thermal cracking)	60	Lima et al. [21]
Palm oil		330–380		75	
Ricin oil		350–400		60	
Soybean oil	Batch-distiller reactor	430	(thermal cracking)	34	Luo et al. [28]
Rapeseed oil				46	
Palm oil	Fixed bed microreactor	450	MCM41	34	Twaiq et al. [32]
Rapeseed oil	“Free fall” reactor	600	(thermal cracking)	7–75	Onay and Kockar [33]
Soybean oil	Tubular reactor (pilot scale)	525	(thermal cracking)	72	Wiggers et al. [35]
Canola oil	Fixed bed microreactor	400	Silica	56	Idem et al. [30]
Soybean oil	Batch-distiller reactor	380–400	calcined bauxite	77	Prado and Filho, [27]
Palm oil	Fixed bed microreactor	350	HZSM-5	28	Twaiq et al. [169]
Canola oil	Fixed bed microreactor	400	HZSM-5	70	Katikaneni et al. [165]
Sunflower oil	Batch reactor	420	HZSM-5	33	Dandik et al. [40]
Rapeseed oil	Batch reactor	350–440	Zeolite NaY and clinoptilolite	85–90	Buzetki et al. [42]
Sunflower oil	Batch reactor	420	Na_2CO_3	47	Dandik and Aksoy [43]
Soybean oil	Batch reactor	340	Al_2O_3	80	Junming et al. [29]
		350–450	Na_2CO_3	81	Junming et al. [44]

higher temperatures, the cracking of the fatty acid chains most likely contributes in a predominant manner.

2.3. Conversion of fatty acids and fatty acids salts

The production of fatty acids as by-products during the processes operating at medium temperatures appears to be a concerning matter in the production of diesel-like fuels. Free fatty acids (FFA) are also present in refined vegetable oils at concentrations less than 0.05%, whereas the FFA content in crude vegetable oils, restaurant waste grease, animal fats and trap greases are in the ranges of 0.3–0.7, 2–7, 5–30 and 40–100%, respectively [49].

Therefore, it is important to consider the operating conditions for converting both the acids and their salts into hydrocarbons. However, fatty acids and/or their salts may also be of interest because they may represent by-products of oil treatments, such as biodiesel production.

According to Billaud et al. [50], octanoic acid only converts by 4% at 450 °C. In the presence of alumina, octanoic acid undergoes a ketonization reaction, which produces 8-pentadecanone with a low conversion at 350 °C and almost complete conversion at 450 °C. Nonanone (most likely from the decomposition of pentadecanone), C_9 and C_{15} hydrocarbons (most likely produced from hydrogen transfer and dehydration of the two ketones) are the other by-products.

At relatively low temperatures (> 350 °C), the carboxylic acid salts also undergo a ketonization reaction that results in chain growth [51], whereas at higher temperatures, liquid fractions are obtained. At 400 °C, calcium decanoate produces a ketonic compound named 10- nonadecanone (nonylnonyl-keton), which undergoes a cracking reaction at higher temperatures to produce the alkyl-nonyl-ketones series. In addition, a further increase of the temperature yields an increasing hydrocarburic fraction with compounds characterized by a number of carbon atoms up to 9.

According to Vonghia et al. [52], who studied the conversion of molecules such as methyl ketones, dodecyl aldehyde, dodecanol on alumina at 450 °C, carboxylic acids ketonize to produce symmetric ketones that subsequently undergo a cracking reaction with a "γ-hydrogen transfer" mechanism, which results in methyl ketones and olefins. Furthermore, the methyl ketones convert to alcohols through hydrogen transfer and dehydrogenation to olefins. A cyclic mechanism or rearrangement of the methyl ketones to aldehydes may occur, which could then produce carboxylic acids with one more carbon atom than the initial carboxylic acid.

According to dos Anjos et al. [39], the conversion of carboxylic acids is less than that of oils in the range of 300–500 °C and using alumina and magnesia.

Ooi and coworkers studied the conversion of fatty acid mixtures derived from palm oil in the presence of the zeolite H-ZSM-5 [53]. The conversion was almost complete at 400–450 °C with a WHSV of 2.51/h and a yield > 60% in a liquid fraction (> 40% gasoline and approximately 30% gases).

Kubickova et al. [54] analyzed the decarboxylation of stearic acid in the presence and in the absence of hydrogen with a Pd/carbon catalyst at 17 bar. At 300 °C in the absence of hydrogen (pure argon), these authors observed a significant decarboxylation (40% conversion after 300 min) with a selectivity towards heptadecane ranging between 60 and 80%; the remaining fraction was composed of unsaturated C_{17} hydrocarbons (olefins and aromatics). The same authors reported similar results in a second study performed with the same catalyst at 360 °C under an argon pressure of 10 bar. They produced C_{17} hydrocarbons, CO and CO_2 [55]. In a subsequent work [56], four different catalysts (Pd on mesoporous carbon) were used in the decarboxylation of stearic and palmitic acid mixtures at 260-300 °C and 17.5 bar, both with and without hydrogen.

The conversion of the tonga oil derived soaps at 400–450 °C was achieved on the industrial scale in China during the Second World War [18]. In recent years, the thermal decomposition of stearic acid calcium salts was studied and compared with tonga oil calcium soaps [57]. Using calcium stearate, the yield in the liquid fraction was significantly greater (76.0%) than that obtained with the soap (41.5%), which produced a considerable amount of carbonaceous residuals (48%).

Recently, Fortes and Baugh [58] chemically characterized the pyrolized products of macauba oil calcium soaps, and they verified the presence of oxygenated compounds, such as aldehydes, ketones, and hydrocarbons.

Doll et al. [34] measured the density, viscosity and superficial tension of an oil obtained by the pyrolysis of a soybean oil derived soap at 350 °C. They obtained values that were comparable to those of petrochemical diesel fuels.

Lappi and Alén [59] recently studied the pyrolysis of some sodium salts; they reported the results with regard to stearic acid, oleic acid and linoleic acid salts using quartz tubes heated at temperatures ranging between 450 and 750 °C and residence times between 20 and 80 s. The conversion was largely incomplete and increased with increasing temperatures and residence times. In all of these experiments, the products contained aliphatic hydrocarbons (paraffins and olefins), aromatics (< 7%) and oxygenated compounds (< 17%). The oxygenated compounds were specifically ketones with a medium molecular weight and aldehydes with a high molecular weight.

Sodium stearate (a salt of a saturated acid) yields fewer aromatics and oxygenated compounds; in contrast, all of these compounds are produced in large quantities by linoleate, which is the most unsaturated salt.

The saponification of vegetable oils before pyrolysis is a plausible solution to limit oxygenated compounds and carboxylic acids in bio-oils and is supported by many authors.

Note that, if the production of carboxylic acids is low, these compounds could be removed using 0.5 M KOH [31]; however, this procedure may not be easy.

2.4. Conversion of animal fats

According to Crossley et al. [60], when working at 300 °C without a catalyst, the primary products obtained from animal fats are free fatty acids and acrolein. When higher operating temperatures (400–500 °C) are used, the cracking phenomenon occurs, which results in the formation of short chain hydrocarbons.

Demirbas [15] reported data on animal tallow, which is commonly used to produce soap, for the production of diesel-like fuels by thermal conversion. The temperature and residence time in the reactor are the two primary operating conditions that were changed. The maximum yield in liquid products was 77.1% when operating at approximately 500 °C.

Adebanjo et al. [16] studied the pyrolysis of swine lard using a fixed bed reactor and flowing N_2 as carrier gas. In this work, the temperature was varied between 500–700 °C. At the lowest temperature, the total liquid yield was near 75%, and the yield decreased by increasing the temperature.

Wiggers et al. [35] studied the continuous pyrolysis of fish oil in a pilot plant. They used a feed rate of 3.2 kg/h and an operating temperature of 525 °C. The obtained yields were: 72.83% in bio-oil; 15.85% in bio-gas and 11.32% in coke. Then, the bio-oil was distilled to obtain 35.86% of light bio-oil, 34.83% of heavy bio-oil and 2.14% of oily sludge.

Chicken fat was thermally treated in the presence of catalysts by Tian et al. [17] in a pilot scale two-stage riser fluid catalytic cracking reactor. The authors used Ultra-Y (USY) and Socony Mobile-Five zeolites as catalysts and operated under atmospheric

pressure at 500 °C in the first reaction stage, and then at 520 °C in the second stage. The hydrocarbon mixture was quite similar to that obtained using palm oil. In a previous work, the same authors [61] examined the behavior of chicken fat at different temperatures with different catalysts (USY, HZSM-5, ANA, Al2O3, and SiO2) in a miniature fixed bed reactor, and they observed a high conversion rate using two acid catalysts (USY and HZSM-5).

2.5. Conversion of glycerol and of byproducts of biodiesel production

Biodiesel production is economically damaged because of the formation of two different byproducts that have a low economic value: glycerin and soap-like residues produced by the neutralization of free fatty acids. Both of these byproducts could eventually be feed to a pyrolysis process.

Glycerin is a material that has a high boiling point (Tb 290 °C under atmospheric pressure, 175 °C at 2 kPa), high density and viscosity, and a low vapor pressure.

In the analyzed studies, a distinction can be made between the results obtained working with pure glycerin, with glycerin/water mixtures and with raw glycerin derived from the Biodiesel production process.

This latter material [62] contains glycerol (70–90%), methanol (< 15%), water (< 15%), inorganic salts (< 5%) and polyglycerol (oligomers, < 5%). Frequently, there are also ethers, which are produced from the reaction of glycerol with methanol, and residual Biodiesel.

Binlin Dou et al. [63] reported that raw glycerin can be diluted with water (10%) to reduce its viscosity and used as a co-feed with combustible oil for thermal station combustors. Furthermore, there are several studies and patents in the literature concerning the conversion of glycerol through thermal pyrolysis and gasification to produce gaseous compounds.

In one of the most recent of these studies [64], the temperature range of 290–310 °C is reported to be the optimal temperature for thermal pyrolysis range; it is also reported that liquid and solid acid catalysts, specifically alumina, are useful in the conversion process.

Binlin Dou et al. [63] recently studied the conversion of crude glycerol (containing methanol and water) and pure glycerol, and they conducted a thermogravimetric analysis of these compounds. During the processing of crude glycerol (with water), a process phase, where a gaseous product (composed of methanol, CO and water) is produced, can be seen operating at 129 °C. Note that the gaseous product was analyzed using IR spectroscopy; consequently, hydrogen was not detected. The main stage of the process is the second one, which occurs between 129 and 203 °C. During this stage, the liquid mass is subjected to a 68% reduction and the emission of methanol, CO, water, CO_2, aldehydes, ethers and other hydrocarbon compounds occurs. After this stage, pure glycerol is reduced to a type of residue that composes only 2% of the total initial mass. However, when using crude glycerol, a residue of approximately 15% of the initial feed is obtained; this residue partially decomposes in the range of 300–530 °C, dropping a further residue of approximately 4%. Operating with these high temperatures resulted in a higher concentration in the gaseous phases of organic oxygenated compounds and CO.

All of these recent studies appear to fully agree with the results of the previous studies by Stein et al. [65]. The authors reported the production of CO, acetaldehyde, acrolein, and then methane and hydrogen were obtained from the thermal decomposition of glycerin.

Corma et al. [47] studied the catalytic conversion of glycerin at 500–700 °C. When using glycerin-water (50–50%) mixtures with high conversion at 500 °C, gaseous yields of approximately 30–50% (CO yield of approximately 10%; CO_2 5–8%; methane 1–4%; ethylene 2–8%; propylene 4–10%; butenes 1–4%) can be observed. All of the cited yields were calculated on a carbonium base catalyst. The remaining products are primarily liquid aromatics (5–10%) and a coke-like residue (40–60%). Higher temperatures resulted in higher gaseous yield and lower "coke" production.

According to Huber et al. [66], when using HZSM-5 (zeolite with medium pores), the amount of produced coke decreases to 20% with an aromatic and olefin yield of approximately 20–50%. Neither the product quality nor the selectivity change when converting a glycerol-vacuum gas oil mixture. These latter results appeared to confirm that adding glycerol to the reaction mixture would not result in further complications in the process but only in an increase of the gaseous fuel production. However, it is also plausible that the addition of glycerin would result in the formation of liquid hydrocarbons or liquid fuels.

3. Conversion of wood and compounds derived from wood

Wood is a material that is primarily composed of three different components: lignin, cellulose and hemicellulose.

The last two components are chemically quite similar because they are composed of oligopolymer sugars (glucose for cellulose and different monosaccharides with five and six carbon atoms for hemicellulose).

3.1. Conversion of cellulose and hemicellulose

In an inert atmosphere and at sufficiently high heating rates [67], cellulose begins to react just above 300 °C. In the range 300–380 °C, there is a development of gaseous molecules with a loss of liquid and solid phases greater than 80%. At temperatures above 400 °C, the further development of gas uses approximately 20–25% of the remaining mass and is accompanied by the progressive evolution of a semisolid material (char) to a bituminous liquid (tar) [68]. The produced bio-oil (tar) primarily contains the depolymerization product of levoglucosan (a highly oxygenated cyclic molecule with six carbon atoms; this molecule is quite similar to glucose with the exception of having two hydrogen and one oxygen atoms) and other highly oxygenated compounds that are derived from glucose.

In a recent study, Lin et al. [69] investigated the transformation mechanism of cellulose. In an anhydrous atmosphere, the first stage of the reaction is the depolymerization, which produces levoglucosan. Subsequently, this compound isomerizes and/or partially dehydrates to produce water vapor and other molecules that belong to the "anhydrosugars" family.

The anhydrosugars undergo a further dehydration to produce furfural and hydroxymethyl furan, which are oxygenated molecules with six carbon atoms and rings with five atoms. Those molecules begin to decompose, producing three-carbon-atom molecules (glycol aldehyde, glyceraldehyde and hydroxyacetone), CO, CO_2 and decarbonylation and decarboxylation products. Some organic products begin to polymerize to produce carbonic species.

Liao et al. [70] reported the formation of several gaseous or volatile compounds other than CO and CO_2; these compounds are primarily methane, hydrocarbons, formaldehyde, hydroxyl acetaldehyde and other aldehydes, ketones and carboxylic acids.

According to Kawamoto et al. [71], the first stage of the depolymerization of cellulose is catalyzed by acid molecules and even occurs at lower temperatures (between 150–200 °C). Some of these catalysts are aluminum trichloride and sulfuric acid.

Dobele et al. [72] also reported ferric sulfate and phosphoric acid, compounds that justify the co-presence of the other components of wood in the catalysis of cellulose depolymerization. A similar result was obtained in the thermal conversion of

paper; nevertheless, in this process, a residual of almost 40% wt/wt was achieved [73]. The studies on the conversion of cotton production byproducts produced similar results [74,75].

Hemicellulose, which is primarily composed of sugar oligomers with five carbon atoms, is even more reactive than cellulose; in fact, it decomposes in the range of 220–300 °C to produce an oily phase that is rich in anhydroxylopyranose (an anhydrosugar with five carbon atoms) [67,68].

In agreement with Peng and Wu [76], during the pyrolysis of hemicellulose derived from corn straw, hemicellulose primarily decomposes in the range 190–315 °C, yielding a residue of approximately 24% wt/wt at 700 °C. The main volatile products are CO_2, acetic acid, furfural, cyclopenthenone derivates and several oxygenated aromatic products.

Corma et al. [47] studied the conversion of an aqueous solution of sorbitol at 500 °C, which is a molecule that is quite similar to glucose and obtainable through the hydrogenation of glucose, with different solid catalysts (with a variable acidity). Conversions of approximately 70% and a gaseous yield of 40–50% were obtained; furthermore, with these operating conditions, a carbonic product (approximately 15%) and aromatics (18–20%) can be obtained. The main gaseous product is CO (yield of 20–25%), with 4–8% of propylene, 2–6% of yield both in CO_2 and ethylene, 2% of butenes, and finally methane, ethane and propane (less than 1% of each of them).

These results seem to confirm that substances composed of sugars and/or cellulose, such as paper, paperboard and residues from food farming productions, may be pyrolyzed.

Considering the high oxygen content in cellulose (49% wt/wt) and the scant number of carbon atoms bonded between each other in glucose (the cellulose monomer), operating with these conversion conditions may predominantly result in the production of light and highly oxygenated fuel molecules (gasoline and gas).

Furthermore, the liquid product could certainly contain additional oxygenated products, and the solid product mass could increase.

3.2. Conversion of lignin and wood

Studies concerning the conversion of wood materials have been reviewed by Mohan et al. [77]. Wood begins to be reactive at approximately 190 °C, and a rapid conversion occurs in the range of 300–400 °C.

According to Paris et al. [78], the decomposition of cellulose micro fibrils occurs in this temperature range. Afterwards, the reactivity of the aromatic nuclei of lignin begins with the formation of strata of graphene (graphite). The maximum amount of liquid products was achieved between 270 and 550 °C, and this amount might be greater than 60% of the initial wood mass. The obtained oils were full of aromatic and phenolic compounds.

Lignin is the primary component in the residuals of the paper production process. This process consists chemical treatments that result in the separation of cellulose from hemicellulose and lignin.

In an inert atmosphere, lignin begins to lose weight above 200 °C, with a loss peak approximately 400 °C [79]. That peak has a tail until temperatures higher than 900 °C. This decomposition produces a residue that is approximately 40% of the initial mass at 900 °C and approximately 50% at 450 °C. During fast pyrolysis at 475 °C, a gas with a yield greater than 30%, an oil with a yield of 53% and a solid with a yield of 15% can be produced. The primary components of bio-oil are polyhydroxy- and/or polymethoxy-benzenes, and sometimes also contains C_1-C_3 alkyl chains and aldehydes.

These compounds are oxygenated aromatics with an oxygen content (w/w) ranging from 13% (4-methyl-cresol) to 35% (syringaldehyde). Compounds such as these are certainly good potential components of a great gasoline; the only possible problem could result from the high oxygen content.

Mullen and Boateng [80] evaluated the total oxygen content in the oil pyrolysis products from wood, straw, grasses and bran in the range of 35–40%. The analysis of the solid residues revealed the partial formation of oxygenated polycyclic aromatics.

As for the volatile compounds produced from lignin pyrolysis, according to Ferdous et al [81] and Shen et al. [79], the formation of water, CO, CO_2, methane, alcohols, phenols and hydrogen was observed.

The production of methanol (which was called "wood alcohol" in the past because of its origin from the industrial high temperature pyrolysis of wood) appears to primarily occur during the second stage of the process, at approximately 380 °C, and it is most likely caused by the cracking of methoxyl groups.

Ferdous et al [81] observed that a gas composed of CO (40%), CO_2 (27%), CH_4 (27%), and superior hydrocarbons (7%) can be produced at 350 °C.

To the best of our knowledge, no studies are reported on the catalytic conversion of lignin at low temperatures.

Thring et al. [82] studied the conversion of lignin in the presence of the HZSM-5 zeolite, starting from a temperature of 500 °C. The authors obtained a gas with a yield of 11%, which was primarily composed of C_3-C_5 hydrocarbons (approximately 64%), CO_2 (10.9%), ethane and ethylene (10%), methane (8.7%), CO and trace amounts of hydrogen. The liquid product was 39% of the starting mass, and it was primarily composed of aromatic hydrocarbons (89%). The remaining solids represented approximately 50% of the starting mass.

As reviewed by Mohan et al. [77], some studies reported the pyrolysis of softwood cortex in a vacuum atmosphere ($P < 20$ kPa). The typical reaction temperature was 450 °C. High density bio-oils were produced (1.09–1.22 kg/l), with a high organic oxygen content that varied between 17 and 31%, a water content of 3–15% and a minimum sulfur content of 0.05–0.07%.

The results available in literature reviews enables the conclusion that adding lignin (as it is or in the form of wood) to the pyrolysis process feed may result in the onset of negative effects due to the production of high quantities of carbonic solids (approximately 30–50% of the mass of the lignin added).

The obtainable liquid product might undergo enrichment to aromatic mononuclear highly oxygenated compounds (phenols, cresols, etc.).

3.3. Conversion of byproducts of crop production and agro-alimentary wastes

Recently, several studies on the thermal conversion of different products, such as seeds, sawdust, shells, hulls, husks, pits, kernels, straw, stalk and various residues, have been published. Many of these materials are mentioned in the recent review by Neves et al. [83]. These materials have intermediate compositions that are typically between those of cellulose and lignin because cellulose, hemicellulose and lignin are their primary components.

As reported by Huang et al. [84], the behavior of several biomasses are properly interpreted as the sum of the behavior of the individual compounds, such as cellulose, hemicellulose and lignin, and the effects of their presence is usually quite limited.

4. Conversion of plastic materials and polymers

Based on an analysis of literature results, numerous studies on the pyrolysis processes on plastic wastes and materials, both catalytic and not, can be found [7–9,85]. These processes are a valid alternative to recycling and could result in obtaining hydrocarbons, mainly in the gasoline range. During such pyrolysis or thermal cracking processes, the plastic materials are heated at high temperatures to decompose their macromolecular structure into smaller molecules, which provides a wide spectrum of hydrocarbon products. For obvious reasons, it is useful to distinguish the behaviors of the different polymers according to the elements that they contain.

In this review, the polymers uniquely constituted by hydrocarbons (polyethylene (PE), polypropylene (PP) and polystyrene (PS)), those containing oxygen (polyethyleneterephthalate (PET) and polymethylmethacrylate (PMMA)), those containing other atoms such as nitrogenated polymers (polyamides and/or nylons, polyacrylonitrile) and those halogenated (polyvinilcloride (PVC)) are considered separately.

4.1. Hydrocarbon polymers: polyethylene (PE), polypropylene (PP) and polystyrene (PS)

The pyrolysis of PE (both LDPE [86] and HDPE [87]) is currently being examined for recovering valuable products and fuels. Depending on the reaction conditions, PE begins to thermally react at 250–450 °C. According to Buekens and Huang [7], non-catalytic conversion occurs at 260 °C, but it is still very slow at 400 °C.

Aguado et al. [88] examined the conversion of LDPE and HDPE, both without catalysts and with catalysts. The term $T_{initial}$ represents the temperature where the degradation begins, and T_{max} is the temperature at which the maximum degradation rate is observed. The authors observed a lower $T_{initial}$ for the samples primarily composed of LDPE (419 °C with respect to 431 °C). This behavior is strictly associated to the highly branched structure of LDPE, which provides a higher portion of reactive tertiary carbons that enhance the initiation step in the degradation reaction [89].

Onwudili et al. [90] recently reported on LDPE pyrolysis experiments conducted in a closed batch reactor under an inert nitrogen atmosphere to study the effects of the reaction temperature and residence time. LDPE was thermally degraded to oil at 425 °C; however, beyond this temperature, the amount of oil product decreased as a result of its conversion to char and hydrocarbon gas. Compositional analysis of the oil products indicated that aliphatic hydrocarbons were the primary components, but the proportion of aromatic compounds increased at higher temperatures and residence times.

Lee [91] reported the formation of a liquid hydrocarbon mixture that was almost free from aromatics from both LDPE and HDPA at 400 °C.

As discussed by Aguado [88], the quality of the catalyst is essentially measured by referring to the lowering of the $T_{initial}$. However, the effect of catalysts on $T_{initial}$ is quite low (generally $\Delta T \sim 50$–75 °C). These authors tested the conversion of both pure and in MSW (Municipal Solid Waste) mixtures of LDPE and HDPE with catalysts such as zeolites (standard ZSM-5, n-ZSM-5 nanocrystalline and Beta), three nano-structured solids (sol–gel Al-MCM-41, hydrothermal Al-MCM-41 and Al-SBA-15) and a non-acid amorphous porous silica used for comparison studies. The standard ZSM-5 zeolite exhibited a low catalytic activity in the degradation of pure LDPE; in fact, the highest degradation temperature for the LDPE/ZSM-5 mixture was observed to be 443 °C, which was only 33 °C lower than the polymer cracking temperature. It can be concluded that the microporous structure and the large dimensions of the crystals hinder the diffusion of large polymeric molecules through the acid sites. In contrast, a higher catalytic activity was observed on pure HDPE, which was most likely due to the lower mean molecular dimensions and the lower degree of branching. These latter two factors are supposed to enhance higher penetration through the pores of the catalyst. In the case of the zeolite Beta, and more markedly for the n-ZSM-5, these type of impediments did not occur and the highest catalytic activities were observed due to the combination of acid properties and a high superficial area. For mesoporous structured catalysts, the disadvantage of having low acid properties is balanced by the presence of large pores that reduce the diffusion barrier.

Zeolites with larger pores, such as UltraStable Y, appear to allow higher liquid yields than medium pore zeolites, as reported by Manos et al. [92], who worked at 360 °C. However, according to other authors, even zeolites with smaller pores, such as ferrierite, may have a high activity in the pyrolysis of polyethylene, which is further enhanced by the generation of secondary mesoporosity by desilication [93].

According to Buekens and Huang [7], in the presence of acidic catalysts, the liquid yield may be $>90\%$ at 400 °C. However, another study [86] indicates that even weakly acidic catalysts, such as silica, allow the production of liquids at 350 °C with a 79% yield, and even basic catalysts, such as MgO, allow a 66% yield of liquids under similar conditions.

Japanese researchers have attempted the selective degradation of polyolefins, including PE, to petrochemical products, such as aromatics, through the use of Ga-ZSM-5 [94–97].

Nishino et al. [98] examined the conversion of high and low density polyethylenes (LDPE and HDPE) and polypropylene (PP), which primarily produced benzene, toluene and xylenes (BTX) with a similar product distribution for every plastic waste mixture analyzed. In this study, the authors used continuous bench-scale reactors (1 kg/h) and pilot-scale reactors (10 kg/h) with Ga-ZSM-5 (Si/Ga=35) as catalysts. Pyrolysis was performed in a range of temperatures from 450–510 °C under atmospheric pressure. More than 80% of the liquid products obtained by Nishino and co-workers [98] comprise aromatics, and precisely, more than 90% of the aromatics were benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene. The gaseous products (30–40% of the total) were primarily composed of light hydrocarbons, C_2–C_4.

Polypropylene is slightly more reactive than polyethylene, which is likely due to its branched structure.

As to the thermal conversion of PP, Wong et al. [99], working at 420 °C, observed a conversion that was one order of magnitude greater than the one obtained at 350 °C. The authors worked in batch systems, and they observed a conversion of approximately 60% at 420 °C and less than 4% at 350 °C. It can be concluded that the reaction temperature has a significant influence on the reaction itself. During the pyrolysis of PP, the above mentioned authors reported the appearance of four different classes of compounds: alkanes, alkenes, dienes and aromatics, with the two former classes present in a larger amount. Furthermore, the product distribution revealed that the majority of the alkenes are in the C_{3n} form, whereas the alkanes are in the C_{3n-1} form and the dienes in C_{3n-2} form. This product distribution can be explained by the typical free-radical mechanism involving bond fission, hydrogen abstraction, β-scission, intramolecular hydrogen transfer, and radical recombination as the dominant steps.

Lee [91] reported the formation of a liquid hydrocarbon mixture by the pyrolysis of PP at 400 °C that was very rich in olefins and naphthenes, and it was essentially free of aromatics. According to Panda and Singh [100], weakly acidic solids such as kaolin and silica-alumina increase the amount of liquid products during the pyrolysis of PP.

Aromatic mixtures, which have a high technical and a low environmental potential, are mainly produced by processing PS and expanded PS plastic wastes, which are compounds that are quite common in the so-called MSW (Municipal Solid Wastes). Chauhan and coworkers [101], through the pyrolysis of such materials, reported a possible achievement of the pyrolysis of liquid styrene; they observed the highest decomposition yield to occur in the range of 350–500 °C, whereas at temperatures lower than 350 °C, no decomposition could be observed. According to the recent paper by Onwudili et al. [90], PS degraded at approximately 350 °C, and the product was primarily a viscous dark-colored oil. The formation of char only increased marginally until 425 °C, but was dramatically enhanced at 450 and 500 °C, reaching up to 30% wt/wt. The oil product from the pyrolysis of PS, even at 350 °C, consisted almost entirely of aromatic compounds, specifically toluene, ethylbenzene and styrene. Under increasing temperatures and residence times, the oil product from PS was preferentially converted into char. Lee [91] also reported the formation of a liquid composed of aromatics with yields $>98\%$ through the pyrolysis of PS at 400 °C.

In the recent work of Wong et al. [99], the non-catalytic pyrolysis of pure PS was analyzed in batch systems (20 mg as feed to the reaction, in the range of 350–420 °C). The complete conversion reached values of approximately 75% at 350 °C, whereas working at 420 °C, maximum values of approximately 90% can be reached after 10 min of reaction, with a subsequent decrease to values of 70% after 180 min.

The main products obtained by Wong et al [99] during the pyrolysis of PS indicate that, at 350 °C, the conversion of low molecular weight compounds reached values of approximately 75%; the predominant products were styrene and 2,4-diphenyl-1-butene (a styrene dimer); their selectivities were substantially independent of the reaction time.

At 420 °C, toluene, ethylbenzene and styrene were also obtained. The styrene selectivity was observed to initially be approximately 70%, and it subsequently decreased with the increasing reaction time, whereas ethylbenzene and toluene selectivities increased in a monotonic way. At these operating temperatures, the secondary reactions of the olefinic compounds were enhanced at higher total pressures. After 180 min of reaction, the pressure reached 4 atm.

4.2. Oxygenated polymers: Polymethylmethacrylate (PMMA) and polyethylene terephthalate (PET)

Polymethylmethacrylate (PMMA) tends to depolymerize to produce the monomer (methylmethacrylate, a liquid with $T_{eb} \sim 373$ K). According to Barlow et al. [102], the thermal depolymerization of PMMA may occur with three different mechanisms depending on the temperature and its molecular weight. At low temperatures (330–400 °C), initiation begins at the chain end, whereas at $T > 400$ °C, random initiation occurs. According to Lopez et al. [103], the pyrolysis of PMMA begins at 280 °C, which is in quite good agreement with Lee [91]. The primary low temperature products are the monomer MMA and ethylacrylate (EA) with maximum yields observed at 400 °C (MMA yield 86.5%, EA yield 6.2%) [103]. At higher temperatures, several other oxygenated compounds are formed.

Kaminsky and Franck [104] and Kaminsky and Eger [105] have investigated the role of fillers in the depolymerization of PMMA, which may cause slightly different yields in the monomer and in the byproducts.

According to Grause et al. [106], the thermal decomposition of PET between 500 and 700 °C does not produce valuable products. Little oil is obtained, and the discharge of carbonic acids, such as terephthalic acid and benzoic acid, cause corrosion and blockages in the processing facilities. Artetxe et al. [107] performed the pyrolysis of poly-(ethylene terephthalate) (PET) in a conical spouted-bed reactor in the temperature range of 500 – 600 °C. The pyrolysis of PET resulted in a high yield of the gas fraction, a small amount of liquids, a significant yield of the solid fraction and a solid residue that remained in the reactor and coated the sand particles.

As described by Yoshioka et al. [108], the pyrolysis of polyethylenetherephthalate (PET), even at moderate temperatures such as 510 °C, produces a small amount of liquids with 38 to 49% yields, and gases that are mostly composed of CO_2 and CO, whereas low quantities of methane, ethane and hydrogen were obtained. The amount aliphatic hydrocarbons in the oil fraction were slight, but the amounts of aromatic hydrocarbons (benzene, benzene derivatives and naphthalene derivatives) were observed to be between 2 and 5% wt/wt of all organic products. At low temperatures (510 °C), benzoic acid, terephthalic acid and monomethyl terephthalate were the main components. Filling materials such as barium ferrite, Fe_2O_3 and NiO exhibited catalytic activity. Specifically, barium ferrite resulted in an increase in the yield of benzene, whereas the basic fillers were observed to cause further decarboxylation.

Martín-Gullón et al. [109] studied the thermal decomposition of PET waste in strict pyrolysis using a batch laboratory scale tubular reactor and operating from 25 to 800 °C. The PET waste was collected from beverage bottles. The material was cut and milled to the appropriate size. Before decomposition, the PET was melted at 250 °C. The pyrolysis began at 400 °C. The thermal degradation was initiated by the random scission of the chain at the ester linkage, which yielded carboxyl and vinyl ester groups [109]. This scission may then produce many different gaseous substances (primary products). The gases formed during the reaction were rich in PAHs (polycyclic aromatic hydrocarbons), but because the PET exhibits high thermal stability, volatile emissions began at temperatures greater than 300 °C.

In the gas, a large number of aldehydes at the low temperature treatments were observed [110]. If the decomposition occurred in an air atmosphere, these primary products can interact with each other or with oxygen to produce secondary products.

To obtain greater amounts of liquid, steam should be added in the pyrolysis reactor. Masuda et al. [111] reported that 56% wt/wt of oil was produced at 500 °C with steam and a goethite catalyst. The oil was composed of 46% wt/wt acetophenone, 28% wt/wt benzene, and 14% wt/wt phenol. The pyrolysis of PET in a steam atmosphere in contact with Ca oxide resulted in the hydrolysis of PET and the subsequent decarboxylation of the resulting terephthalic acid. While the hydrolysis proceeded well at temperatures below 500 °C, the decarboxylation proceeded with a sufficient velocity at approximately 500 °C and produced a high yield of benzene. The best results were achieved at a heating rate of 2 K/min between 300 °C and 500 °C, which produced a benzene yield of 74% with a purity of 97% wt/wt [112].

Polyoxymethylene (POM) thermally depolymerizes to produce formaldehyde and its oligomers in the range of 300–420 °C [113].

4.3. Polyvinyl chloride (PVC)

The pyrolysis of PVC occurs in two steps. The reaction begins near 250 °C, resulting in the thermal dehydrochlorination that removes more than 93% of chlorine as gaseous HCl in the 250–400 °C range [114–117]. This step produces a liquid with a yield of 50–65% wt/wt that is composed of 60–80% aromatics (benzene, toluene, naphthalenes, indenes, etc. [113]) and that still contains 0.5–1% of chlorine wt/wt. According to Ragazzi et al. [117], during the first step that occurs in the 220–370 °C interval, benzene is evolved with HCl, whereas during the second step in the range of 400–530 °C, many gaseous products are produced. The cracking of the resulting molecule produces a number of light

hydrocarbons, such as alkanes and olefins, as found in other recent studies [118].

4.4. Nitrogen containing polymers

In the past 50 years, among the various nitrogen containing compounds, nylon-6 has been decomposed through thermal degradation or pyrolysis (300–500 °C), specifically for the recovery of caprolactam, which is its highly valuable monomer [119–121]. The thermal decomposition results in the evolution of ammonia and HCN in the gas phase [122]. Czernik et al. [119] studied the effect of operating parameters, such as temperature (between 330 and 360 °C) and the type of catalyst, in a microreactor coupled with a molecular beam mass spectrometer. Catalytic pyrolysis was performed using an alumina catalyst supported on KOH. This type of process had an elevated velocity and high selectivity. Only a few minutes were necessary to depolymerize nylon-6 and to obtain high yields of caprolactam (85%). A similar result was also obtained by Lee [91] through the pyrolysis of nylon-6 at 380 °C.

Studies on the thermal non-oxidative degradation of nylon 6,6 were reviewed by Schaffer et al. in 2000 [123]. The thermal decomposition of nylon 6,6 results in the evolution of CO_2, ammonia and HCN in the gas phase [122]. Several products have been observed to form in the low temperature range, 180–300 °C. The majority of these products are N-containing hydrocarbons, such as n-hexylamine, n-pentylamine, and hexa-methylendiamine, which are usually present with cyclopentanone.

Lee [91] also investigated the pyrolysis of styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) copolymers. The decomposition of these two elastomers is even faster at 380 °C and produces a mixture of aromatic hydrocarbons and N-containing compounds (40–43%). The main products from the pyrolysis of ABS are reported to be styrene and 4-phenylbutyronitrile [124,125]. When using silica-alumina and iron oxide catalysts, the production of 4-phenylbutyronitrile decreases [125].

The thermal decomposition of polyurethanes in an inert atmosphere has been widely studied as a method for recovery and recycling [126]. These materials decompose in the range of 150–350 °C [127,128] primarily by depolymerization (reproducing diisocyanate and diol), and by decomposition to produce CO_2 and diamine or amine+olefin. this process produces a gas phase that contains CO_2, HCN and very complex mixtures of many oxygenated and nitrogenated compounds [129,130].

A study by Rogaume et al. [131] addressed the pyrolysis of PUF foam from automobile seats. First, thermogravimetric and calorimetric (TGA/DTA+DSC) tests were performed under a flow of air. Mass loss begins at ~250 °C and levels off at a mass loss of ~80% at 300 °C, whereas the remaining 20% is not decomposed until the temperature reaches 500 °C. The DSC results reveal several exothermic peaks; the most important peak occurs at 250–300 °C and others at the start (340 °C) and end (490 °C) of the second decomposition stage [128,132]. RIM PU pyrolysis typically gives (at >450 °C) 5–25% wt/wt char, 10–45% wt/wt liquids and >40% wt/wt gases. The liquid is a red-colored, viscous and single-phase oil with a viscosity that increases with time. To increase the amount, quality and marketability of the liquid product, the use of activated carbon and PU chars in a secondary pyrolysis reaction step was examined [133].

Font et al. [134] focused on the degradation kinetics. For this purpose, they used a thermobalance and a laboratory furnace for the evaluation of gaseous and volatile compounds. The yield of light hydrocarbons (methane, ethane, ethylene, etc.) increased as the pyrolysis temperature increased (500, 600, 700, 800 and 900 °C). The yield of benzene varied between 8 to 14% wt/wt; the yield of methane was from 5 to 7% wt/wt; the yield of ethylene was between 11 and 14% wt/wt; 2.9% wt/wt of HCN was obtained. Considerable amounts of ammonia (6% wt/wt), styrene (1.4% wt/wt), aniline (0.55% wt/wt), benzonitrile (0.6% wt/wt), 1-propenyl-benzene (1% wt/wt) and naphthalene (1.5% wt/wt) were obtained at 850 °C. The yield of the residue varied from 69 to 29% wt/wt, and no correlation between the char yield and the temperature was observed.

4.5. Mixed polymeric materials and mixed plastic wastes

Many studies have examined the pyrolysis of mixed polymers. While it appears that different polymeric materials usually behave quite independently from each other, in some cases, interesting interactions have been observed. In a mentioned study of Wong et al. [99] the behavior of the binary mixture PS/PP was investigated. In the case of the binary mixture, the conversion of PS remained essentially the same, whereas a marked increase was observed for the conversion of PP. This aspect highlights the fact that the degradation of PP can be enhanced by taking advantage of the synergic effects due to the use of PS.

According to Onwudili et al. [90], during the co-pyrolysis of a 7:3 mixture of LDPE and PS, a wax product was observed at 350 °C that resulted in an oil at 400 °C, which indicates that the presence of PS influenced the conversion of LDPE by lowering its degradation temperature. The mixture produced more oil and less char than the individual plastics at 450 °C.

Similarly, Szabo et al [135] studied the pyrolysis of PMMA-ABS mixture wastes, which produced liquids containing nitrogen and oxygen compounds. The interactions between PMMA and ABS appear to modify the decomposition characteristics of the ABS, which results in a lower degradation temperature than that of pure ABS. Furthermore, the simultaneous decomposition results in the recombination of the products, which yields new volatile compounds.

The effect of mixing is particularly important when PVC is present in the mixture. In this case, the greater the PVC content, the higher the chlorine concentration in the produced liquids [136].

Real polymeric wastes are usually quite complex mixtures. For example, rubber materials are complex copolymer mixtures that also contain chlorinated and nitrogenated polymers and, if vulcanized, also contain significant amounts of sulfur. Furthermore, these substances are often used as filling additives (carbon dust and/or silica and/or kaolin) and can contain supporting metal structures.

Laresgoiti et al. [137] studied the effect of temperature from 300 to 700 °C on the pyrolysis of tires. They observed that temperatures higher than 500 °C did not influence the yields of the products. In agreement with the previous authors, Barbooti et al. [138] concluded that the optimal temperature for the pyrolysis of tire wastes to produce oil and carbon is 430 °C.

Qu et al. [139] examined the co-pyrolysis of tire wastes on the ZSM-5 zeolite with a lubricant base oil (LBO) at 430 °C under an inert atmosphere and in a bench scale reactor. The addition of LBO resulted in an increase in the degradation velocity and the liquid yield (from 33.6% without using LBO to 48.0% using LBO), whereas the yields of gases and wastes decreased. During the pyrolysis of oils, the amount of heavy compounds decreased and the amount of light components (n-C < 12) increased; specifically, the amount of compounds with C_{10} significantly increased. It was observed that the use of LBO (10 g of tire wastes mixed with 0.005 g of ZSM-5 and 0.005 g of LBO in a 60 ml volume reactor) enhanced the interaction between the tire wastes and the catalyst, which resulted in an improvement in the pyrolysis velocity and the yield of valuable compounds. The tires decomposed into gaseous and

liquid products, which can be used as fuels and raw materials for chemical industries.

However, a commercial pyrolysis of tires requires precise optimization processes, which several authors have dedicated a considerable amount of work [140–143].

Williams and Brindle [140,141], for example, have proposed a two-step pyrolysis process to increase the concentration of raw materials during pyrolysis for the utilization of this process by chemical industries.

Note that the oils from the pyrolysis of tire wastes have a sulfur content due to the vulcanization treatment of the tires. Qu et al. [139] reported this value to be 0.8%, which is comparable with commercial diesel standards. However, the nitrogen and chlorine contents are relatively greater than that in diesel. As for the liquid product distribution, the carbon numbers in products are from C_4 to C_{20} with an average carbon number of 10.5. The most abundant products are 1, 2-dimethylcyclopropane, pentadiene, hexadiene, dimethylpentadiene, phenylbutene, toluene, ethylbenzene, xylenes, styrene, cumene, propylbenzene, 1-ethyl-3-methylbenzene, methylstyrene, cymene and limonene; limonene occurs at the highest concentration (8.08%). Limonene is the main constituent of citrus oil and has extremely fast-growing and wide industrial applications, such as dispersing agents for pigments, feedstock for the production of fragrances and flavorings, etc. This compound is primarily derived from the thermal decomposition of polyisoprene, which accounts for approximately 50–60% of the typical truck tire formulation [144].

In addition, similar to the findings reported by Qu et al. [139], Yanik et al. [145] had already identified that the co-pyrolysis of municipal plastic wastes was favored by the presence of heavy vacuum gas oil (HVGO). The liquid yield increased because HVGO acts as a solvent and ensured homogeneity conditions, and it prevents repolymerization and the formation of gases during the degradation of MWP.

The primary problem associated with hospital wastes is generally associated with a high PVC content, which produces liquid fuels contaminated by chlorine during pyrolysis. The recent studies of Lin et al. [146] and Huang et al. [147] on the pyrolysis at 390 °C with catalysts such as FCC-R1, Silicalite, HUSY, ZSM-5 and SAHA (amorphous silico-alumina), confirm that the thermal decomposition leads to hydrocarbons from plastic wastes mixtures (mainly made of polyethylene, polypropylene, polystyrene and polyvinyl chloride.

Two recent reviews [148,149] have reported data on the pyrolysis of Automotive Shredder Residue (ASR), which is an important residue that contains different plastics. The considerable heterogeneity of this material hampers technologies for the production of liquids from it and the utilization of the very impure char resulting from its treatments [150].

Therefore, the pyrolysis of ASR is mostly performed at high temperatures to convert it into gases.

Zolezzi et al. [151] reported the production of 35% of liquids containing 1% N and S after pyrolysis at 500 °C under fast pyrolysis conditions (5 °C/s, solid residence time 5–8 min).

De Marco et al. [152] reported results from a treatment at 400 °C in an autoclave under nitrogen flow at a heating rate of 15 °C/min with hold at 400 °C for 30 min. Starting from "light ASR", the yield of the liquid product is only 7.1%, and it contains 70% water. When starting from "heavy ASR", the yield of the liquid product is 25.5% and contains 18.2% water; the organic product contains 85.2% carbon, 10.4% hydrogen, 1.1% nitrogen and 0.3% sulfur.

Noureddine [153] and Donaj et al. [150] reported data concerning a microwave pyrolysis process operating at 300 °C in the presence of steam, which produced a liquid as the main product. A summary of the primary medium-temperature thermal and catalytic pyrolysis studies of plastic wastes and materials is presented in Table 4.

5. Mixed wastes

Municipal solid waste (MSW) mainly consists of household and commercial wastes, which are disposed of by, or on behalf of, a local authority. MSW is mainly composed of paper/cardboard, plastics, glass, metals, textile and food/garden waste. Consequently, the waste contains a high proportion of renewable materials that can be used for energy recovery or the production of solid, liquid and gaseous fuels [154].

Buah et al. [154] used the municipal solid waste in the form of long pellets (with a 16 to 80 mm diameter) of refuse-derived fuel. The pellets were obtained by removing all of the compounds that would lower the calorific value of the product (such as glass, metals, putrefying material, etc.). They used a fixed bed reactor, matrix particle sizes from 0.5 to 3.3 mm and the pyrolysis temperature was increased from 400 °C to 700 °C. When increasing the temperature, the yield of liquids was increased from 30 to 50%, and the yield of gas was increased from 18.6 to 20.1%, whereas the content of coke in the product decreased from 49.8 to 32.3%. Similar results were obtained by other authors for the pyrolysis of MSW [155–157]. For example, Lin et al. [157] used refuse-derived fuel (RDF) at 500 °C, and they obtained 28% of liquids, 30% of gases and 42% of solid residues. Similar yields were observed by Rampling and Hickey [156], who varied the temperature from 300 to 700 °C in a batch mode using a fixed bed reactor. The liquid and gas yields increased from 32 to 49% and from 18 to 22%, respectively. Roy et al. [155] obtained a 35% yield of fuel oil with tar by using temperatures lower than 450 °C in a vacuum reactor.

Pyrolysis of a mixture containing polyethylene (PE), polypropylene (PP) and polystyrene (PS) in the form of pellets, pine sawdust and used tires were studied by Paradela et al. [158]. The best operating conditions were as follows: reaction temperature of 420 °C, reaction time of 20 min and waste mixture composition with 80% (45% PE, 14% PS, and 21% PP) plastics, 10% wood and 10% tires. The increase of the plastics content in the blend increased the yield of the liquids (from 33% to 92% wt/wt). The conversion of aromatic compounds into alkanes and alkenes was also favored by increasing the plastic wastes in the blends, which decreased the contents of aromatic compounds from 52% to 28% wt/wt. Furthermore, a decrease of CO_2 production in the gaseous phase (from 67% to 2% v/v) was observed, whereas the release of hydrocarbons increased, which resulted in a gas with a higher energy content.

Phan et al. [159] pyrolyzed waste wood, cardboard or textile residues in a small packed bed reactor at a final temperature ranging from 350 to 700 °C with a slow heating rate. They calculated the yield of liquid, gas and solid residue wastes, and the products were analyzed by GC–MS (liquid and solids) and GC (gases). The authors mentioned that carbon residues contained approximately 38–55% of the energy content in the raw material, whereas the liquids contained only 20–30%. The liquids mainly consisted of water (approximately 33% of the raw material) and oxygenated compounds, such as furans (derivates from carboxylic acids and polysaccharides). The produced gases were primarily CO and CO_2 with increasing proportions of CH_4 and H_2 with the increase of temperature. To obtain a good compromise between the "char" and liquid, the authors suggested temperatures below 500 °C.

Cellulosic materials (paper, cardboard and wood), plastics (polystyrene, polypropylene, low-density polyethylene and high-density polyethylene) and mixed materials from MSW (juice containers comprising: cardboard (75%), plastics (20%) and aluminum (5%) were employed by Sørum et al. [160]. The samples were heated at a constant rate of 30 °C/min up to 110 °C to remove the present water. After a drying period of 30 min, the

Table 4
Summary of main medium-temperature pyrolysis studies of plastic wastes and materials.

Substrate	Description	Temperature (°C)	Catalyst	Main yields (%wt/wt)	Reference
LDPE	Closed batch reactor under nitrogen atmosphere	425	(Thermal cracking)	Liquid: 89.5 Gas: 10.0	Onwudili [90]
Municipal plastic waste (MPW)	Stirred semi-batch reactor in the absence of oxygen	400	(Thermal cracking)	Low MPW: Liquid: 89.9; gas: 11.1 Medium MPW: Liquid: 89.8; Gas: 2.9 High MPW: Liquid: 76.0; Gas: 9.7	Lee [91]
HDPE	Ultrastable Y zeolite in semi batch reactor	360	Ultrastable Y zeolite	Liquid: 46	Manos [92]
LDPE	Batch reactor under atmospheric pressure	350	SiO_2; MgO	Using SiO_2 and 3 h liquid yield: 79; using MgO and 2 h liquid yield: 66	Shah [86]
LDPE-HDPE	Continuous bench/pilot-scale reactor and Ga-ZSM-5 as catalyst	450–510	Ga-ZSM-5	Liquid: 80 Gas: 30–40	Nishino [98]
PE/PP	Isothermal fluidized sand bath reactor	420	sand	Total conversion: 60	Wong [99]
Expanded PS	Bench-scale reactor using ceramic pebbles of sizes 1.27×10^2 m to 2.54×10^2 m, vacuum conditions	500	(thermal cracking)	Liquid: 91.7	Chauhan [101]
PMMA	Conical spouted bed reactor with nitrogen to fluidize the bed	400	(thermal cracking)	MMA: 86.5 EA: 6.2	Lopez [103]
PET	Calcium oxide filled column	300–500	CaO	Benzene yield: 75% with the purity of 97 wt%	Grause [106]
PET	Conical spouted-bed reactor	500–600	(thermal cracking)	High yield of gas; low amount of liquid; significant yield of solid	Artetxe [107]
PET	Fluidized bed reactor	510	quartz sand	Liquid: 2–12 Gas: 38–49	Yoshioka [108]
PVC	Two steps pyrolysis	250–400	(thermal cracking)	Liquid: 50–65	German [113]
Nylon-6	Bench-scale fluidized bed reactor with a-alumina supported KOH	330–360	α-alumina supported KOH	Caprolactam yield: 85	Czernik [119]
SAN ABS	Stirred semi-batch reactor in the absence of oxygen	380	(thermal cracking)	Aromatic hydrocarbons and N-containing compounds: 40-43	Lee [91]
RIM PU	Batch- laboratory scale reactor with a packed carbon bed	>450	Activated carbon	Liquid: 10–45 Char: 5–25 Gas: >40	Takamoto [133]
Tire waste	Bench-scale reactor on ZSM-5 Zeolite with lubricant base oil under inert atmosphere	430	ZSM-5 Zeolite	Liquid: 48	Qu [139]
ASR	Fast pyrolysis	500	(thermal cracking)	Liquid: 35 Gas: 7.7 Solid: 47.5	Zolezzi [151]
ASR	unstirred stainless steel 3.5 m^3 autoclave under nitrogen atmosphere	400	(thermal cracking)	Liquid: 25.5 Gas: 20.4 Solid: 54.1	De Marco [152]

samples were heated to the desired temperature (500 or 600 °C) at the pre-selected heating rate of 10 °C/min. The authors examined the mass losses of the treated samples and the calorific value of the produced gases. For the cellulosic fraction, the maximum vapor production was achieved at 360 °C with a calorific value between 19 and 10 MJ/kg. The plastic materials were degraded

Table 5
Average temperature threshold for fast thermal decomposition of biomasses and plastics.

Compound	*T* threshold (°C)	Main primary liquid product
Triglycerides	300–400	Linear hydrocarbons, oxygenated compounds
Cellulose	320	Levoglucosane, oxygenated compounds
Hemicellulose	190	Anydroxylopiranose, oxygenated compounds
Lignin	200	Oxygenated aromatics (phenols, methyl- and methoxy-phenols, hydroxybenzaldehydes)
LDPE	420	Linear paraffins and olefins
HDPE	430	Linear paraffins and olefins
PP	350	Branched paraffins (propylene oligomers)
PS	330 – 380	Styrene monomer, styrene dimer
PMMA	280	Methylmethacrylate monomer
PET	400 8	Oligomers (vinylesters), aromatic hydrocarbons
PA6	330	ε-caprolactam
PA66	250–300	Amines, cyclopentanone, hydrocarbons.
PU	300	Diisocyanates, diol, diamine, amine, olefins, benzene, naphthalene,
SAN, ABS	380	Nitriles, aromatic hydrocarbons
PVC	300	Hydrocarbons, chlorided hydrocarbons.

Table 6
Analytical composition of common materials and wastes.

Compound	Ultimate analysis% wt/wt								Ref.
	C%	H	O	S	N	Cl	Ash	d&af [a]	
Vegetable cooking oil	76.36	11.62	12.02	$9\ 10^{-5}$	$6{,}9\ 10^{-5}$	–		x[b]	[45]
Used cooking oil	76.74	11.62	11.63	0.0038	0,0047	–		x	[45]
Lard	77.4	11.5	10.4	0.1	0.6	–	–	x	[176]
White grease	77.9	13.6	8.1	0.2	0.2			x	[176]
	76.5	11.5	11.6	0.007	0.05	–		x	[177]
Yellow grease	76.4	11.6	12.1	0.005	0.03	–		x	[177]
Chicken fat	75.3	11.4	13.1	0.006	0.04	–		x	[177]
Tallow	76.6	11.9	11.4	0.003	0.02	–		x	[177]
Chicken litter	60.5	6.8	25.3	1.2	6.2	0.5 db		x	[163,178]
Meat bone meal	57.3	8.0	20.8	1.69	12.2	0.87 db		x	[163,178]
α-cellulose	44.44	6.17	49.38	–	–	–		x	[179]
Cellulose wadding	36.37	5.08	41.85	–	< 0.1	–			[180]
Glossy paper	41.9	5.3	52.59	0.02	0.1	0.093		x	[181]
Cotton	44.92	9.00	45.86	0.03	0.19	–	–	x	[182]
Lignin (paper ind.)	61	7	31	< 0.03	0.9	–	–	x	[183]
Kraft lignin	59.92	5.9	32,54	–	1.62	–	2.3		[81]
Alcell lignin	66.41	5.98	27.25	–	0.21	–	0.15		[81]
Lignin (bioethanol ind.)	54.28	6.11	39.44	0.17	0.9	–	–	x	[183]
Wood, bark, sawdust	57.0–48.7	10.2–5.4	45.3–32.0	0.41–0.01	0.7–0.1	0.05–0.01 db		x	[163, 184, 185]
Grasses	52.0–46.1	6.5–5.1	44.5–42.5	0.27–0.04	2.6–0.3	0.83.0.04 db		x	[163,184,186]
Straws	50.6–48.5	6.4–5.6	44.6–40.1	0.28–0.08	2.8–0.5	0.64–0.03 db		x	[163,184,186,187,188,189]
Hulls, shells, husks, pits, kernels	58.4–42.2	9.2–3.2	49.0–34.2	0.60–0.01	3.4–0.1	0.21–0.01 db		x	[163,184,190,191,192,193]
Demolition wood	48.29	6.08	44.13	0.09	0.38	0.03		x	[181]
Mushroom waste	40.24	5.05	53.09	0.19	1.43	–		x	[180]
Coffee waste	51.33	6.79	38.60	0.21	3.02	0.05		x	[181]
Marine macroalgae	43.2	6.2	45.8	2.6	2.2	3.34 db		x	[163,194,195]
LDPE	67.20	9.70	15.8	0.07	0.46	–	6.64		[196]
HDPE	84.38	14.14	–	0.03	0.06	tr	1.19		[196]
PS	86.91	8.42	3.96	0.02	0.21	tr	0.45		[196]
PET	62.5	4.14	33.1	–	–	–	0.5		[196]
PU	63.14	6.25	17.61	0.02	5.98	2.42	4.38		[196]
PU (TDI + PPG)	60.6	8.2	27.9	3.3	–			x	[130]
PVC	41.55	4.81	–	0.02	0.09	52.95		x	[115]
PVC	44.4	5.7	–	–	0.2	36.3			[116]
PVC wires	38.6–40.9	3.7–5.6	–	–	4.6–9.5	44–53		x	[197]
Automotive shredder residue	49.5	5.3	6.9	0.2	4.5	0.5	36.2		[198]
	56.6	7.9	21.4	2.7	0.2	–	12.1		[199]
Hospital plastic waste	84.84	12.32	0.06	0.132	0.07	2.72		x	[146]
Used tyres	74.5	6.00	3.00	1.50	0.50	1.00	13.5		[139]
Waste lubricant oil	83.6	13.2	–	0.52	0.10	–	–		[200]
Sewage sludge	50.9	7.3	33.4	2.3	6.1	0.04 db		x	[163,187,190]
Refuse derived fuel	53.8	7.8	36.8	0.47	1.1	0.83		x	[163,184,201]

[a] Dry and ash free.
[b] Dry basis.

from 350 to 500 °C, which resulted in a calorific value ranging from 42 to 47 MJ/kg.

The low-temperature pyrolysis of putrescible garbage (PG) and solid fraction of sewage sludge (SS) was investigate by Shen and Zhang [161]. They used two rotary kiln type reactors in series, where reaction temperatures between 400 and 550 C and solid retention times of 20 and 60 min were employed. The authors used different ratios of PG, SS and ash produced from sewage sludge after pyrolysis: 80:20:00, 80:20:20, 60:40:00, 60:40:20, and 60:40:50. These samples were pelletized to form agglomerates that were 3–5 mm in diameter and dried in an oven for 24 h at 70 °C. The maximum yield of oil (22%) was achieved at 550 °C using 60:40:50 (PG:SS:ash). It was observed that putrescible garbage tends to produce oils with a higher viscosity, whereas the addition of sewage sludge significantly increases the oil yield and reduces the oil viscosity. Furthermore, the addition of sewage sludge ash to the feed mixtures reduces the oil viscosity, which reveals the catalytic characteristics of the ash in cracking the oil.

The catalytic pyrolysis of sewage sludge in a fluidized bed reactor using emery (Al_2O_3, (Nanko Abrasives, Japan)) as a catalyst was studied by Park et al. [162].The results indicate that the optimal temperature for bio-oil production is 450 °C and particle sizes between 0.3 and 1 mm.

6. Concluding considerations

In the previous chapters, we analyzed literature data concerning the thermal and catalytic conversion of different organic matrices under similar conditions. Our interest was focused on the best conditions to obtain liquid products that could possibly be used as fuels.

In Table 5, the temperatures where the single pure components of solid wastes and biomasses begin to become reactive and decompose are reported. It is evident that in the temperature range of 300–400 °C, most of the organic matrices begin to be reactive and decompose to produce gaseous and liquid products. The compounds that decompose in this range are the most reactive, i.e., those containing functional groups and essentially relevant amounts of heteroatoms. These materials are biomasses and oxygenated, nitrogenated and chlorinated polymers.

The most refractory compounds to decompose are polyolefins, such as PE and PP, which require a significantly higher temperature (i.e., 400–450 °C) to be converted at a significantly high rate. However, at this temperature, the cracking tends to be so strong that it tends towards the production of gases.

A relevant factor to be taken into consideration, in particular in relation to the quality of the liquid and gaseous products, is the elemental composition of the material to be used (see Table 6). The lower the heteroatom content (i.e., the lower the oxygen, nitrogen, sulfur and chlorine content) in the raw material, the best properties of the obtained liquid are to be expected. Therefore, the pyrolysis of polyolefins, such as polyethylene, polypropylene, polystyrene, polyisobutene, polyisoprene and polybutadiene, although being harder, i.e., obtained at higher temperature, is expected to produce essentially pure hydrocarbon fuels and byproduct gases.

However, it has to be considered that wastes based on these polymers may contain heteroatoms as additives. This is the case of sulfur in vulcanized rubber and tires. This sulfur is present in liquids obtained by the pyrolysis of rubber. Rubber may also contain chlorinated polymers; therefore, chlorine may be present in the pyrolysis liquids.

As for biomasses, the majority of them have a significantly low nitrogen, sulfur and chlorine content, but they always have a significant oxygen content. Vegetable oils are almost always free of N, S and Cl, and they also have a quite low oxygen content (ca. 12% d&af, see Table 6), thereby allowing the production of high hydrocarbon fuels with a moderate oxygen content. Vegetable oils are also free of aromatics and contain medium-long aliphatic hydrocarbon chains, thereby allowing the production of liquids that have good cetane numbers if they are converted at moderate temperatures. Animal fats may behave even better in this sense because they have more saturated acid chains than vegetable oils.

Used frying oils may have more sulfur and nitrogen, but these elements are still in low concentrations, thereby also allowing the production of good quality fuels. Animal fat also has a similar composition with very small amounts of sulfur and nitrogen. Therefore, it is evident that biomasses based on triglycerides are good raw materials for producing good quality oils through medium temperature pyrolysis. The moderate presence of oxygenated compounds, and in particular of carboxylic acids, is the main problem in this case.

Recently, Vassilev et al. [163] reviewed the chemical composition of a significant number of different biomasses, primarily lignocellulosic. The oxygen content of these materials is always in the range 32–49% (d&af). This range is limited by the value of cellulose, which is may be above 50% (theoretical value 49.4%) and that of lignin which is usually near 30%. In normal woody biomasses nitrogen content is lower than 1%, sulfur content is lower than 0.5% and chlorine content is lower than 0.05% (dry basis). However, a slightly different situation occurs with grasses and straw, in which nitrogen can reach 3%, and chlorine can reach 0.8% (dry basis). Grasses and straw may also contain significant amounts of silicon.

In any case, it is evident that the high amount of oxygen present in both cellulose, hemicellulose and lignin, and the important amounts of aromatics typical of lignin, will give rise to pyrolysis liquids that are very rich in oxygenated aromatic compounds. These liquids may have good anti-knocking properties, but still have too much oxygen and would also contain some sulfur, nitrogen and chlorine. Catalytic upgrading, such as hydrotreating, may strongly improve the quality of the bio-oils [164], but this step, obviously, implies a deep complication in most processes.

The pyrolysis of nitrogenated polymers (polyurethanes, polyamides) whose N content can be as high as 5–8% together with $>15\%$ oxygen, results in nitrogen and oxygen containing liquids.

The presence of chlorine is also very relevant. This presence is mostly derived, in wastes such as medical plastic waste, from PVC, which contains $>45\%$ of chlorine by weight (theoretical value 56.8%). However, significant amounts of chlorine can also be found in rubber (polychloroprene) used solvents and in a much lower extent in grasses, straw and paper.

It is evident that medium temperature pyrolysis may be an interesting technology to recover energy from wastes and biomasses, as well as to reduce the volume of wastes to be disposed. However, liquids produced (and gases as well) will contain, depending on the raw material, quantities of heteroatoms that further purification treatments maybe necessary to limit pollution from the process.

A further question concerns the use of catalysts to obtain biomass and waste pyrolysis. Catalysts, in particular acid catalysts, seem to favor the pyrolysis phenomenon to a significant but limited extent. On the other side, catalysts are also somehow poisoned by some of the components of the biomass and of the resulting bio-oils. These poisons are likely mostly basic compounds such as ammonia and amines, but oxygenates can also participate. This could make necessary recovery and regeneration of the catalysts, which is sometimes not really possible. This may be the case of raw materials containing relevant amounts of ash, such as most biomass residues and industrial wastes. In this case, to make the process economically feasible, very cheap catalytic materials could be used, if any, without recovery. These problems might make thermal pyrolysis more attractive than catalytic one in many cases.

References

[1] Naik SN, Goud VV, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. Renewable & Sustainable Energy Reviews 2010;14:578–97.
[2] Demirbas A. Competitive liquid biofuels from biomass. Applied Energy 2011;88(1):17–28.
[3] Swain PK, Das LM, Naik SN. Biomass to liquid: a prospective challenge to research and development in 21st century. Renewable & Sustainable Energy Reviews 2011;15(9):4917–33.
[4] Damrtzis T, Zabaniotou A. Thermal conversion of biomass to second generation biofuels through integrated process design—a review. Renewable & Sustainable Energy Reviews 2011;15:366–78.
[5] Manganaro J, Chen B, Adeosun J, Lakhapatri S, Favetta D, Lawal A, Farrauto R, Doraio L, Rosse DJ. Conversion of residual biomass into liquid transportation fuel: an energy analysis. Energy and Fuels 2011;25:2711–20.
[6] Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: a review of subcritical water technologies. Energy 2011;36(5):2328–42.
[7] Buekens AG, Huang H. Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. Conserve Resources Recycling 1998;23:163–81.
[8] Al-Salem SM, Lettieri P, Baeyens J. Recycling and recovery routes of plastic solid waste (PSW): a review. Waste Management 2009;29:2625–43.
[9] Al-Salem SM, Lettieri P, Baeyens J. The valorization of plastic solid waste (PSW) by primary to quaternary routes: from re-use to energy and chemicals. Progress in Energy and Combustion 2010;36:103–29.
[10] Karmakar A, Karmakar S, Mukherjee S. Properties of various plants and animals feedstocks for biodiesel production. Bioresource Technology 2010;101:7201–10.
[11] Schwab AW, Bagby MO, Freedman B. Preparation and properties of diesel fuels from vegetable oils. Fuel 1987;66:1372–8.
[12] Ali Y, Hanna MA. Alternative diesel fuels from vegetable oils. Bioresource Technology 1994;50:153–63.
[13] Maher KD, Bressler DC. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. Bioresource Technology 2007;98:2351–68.
[14] Demirbas A. Progress and recent trends in biodiesel fuels. Energy Conversion and Management 2009;50:14–34.
[15] Demirbas A. New liquid biofuels from vegetable oils via catalytic pyrolysis. Energy Education Science and Technology 2008;21:1–59.
[16] Adebanjo AO, Dalai AK, Bakhshi NN. Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat. Energy and Fuels 2005;19:1735–41.
[17] Tian H, Li CY, Yang CH, Shan HH. Alternative processing technology for converting vegetable oils and animal fats to clean fuels and light olefins. Chinese Journal of Chemical Engineering 2008;16:394–400.
[18] Chang CC, Wan SW. Chinas motor fuels from tung oil. Industrial & Engineering Chemistry 1947;39:1543–8.
[19] Schwab AW, Dykstra GJ, Selke E, Sorenson SC, Pryde EH. Diesel fuel from thermal decomposition of soybean oil. Journal of the American Oil Chemists Society. 1988;65:1781–5.
[20] Idem RO, Katikaneni SPR, Bakhshi NN. Thermal cracking of canola oil: reaction products in the presence and absence of steam. Energy and Fuels 1996;10:1150–62.
[21] Lima DG, Soares VCD, Ribeiro EB, Carvalho DA, Cardoso ECV, Rassi FC, Mundim KC, Rubim JC, Suarez PAZ. Diesel-like fuel obtained by pyrolysis of vegetable oils. Journal of Analytical and Applied Pyrolysis 2004;71:987–96.
[22] Fortes ICP, Baugh PJ. Study of analytical on-line pyrolysis of oils from Macauba fruit (*Acrocomia sclerocarpa* M.) via GC/MS. Journal of the Brazilian Chemical Society 1999;10:469–77.
[23] Fortes ICP, Baugh PJ. Pyrolysis-GC/MS studies of vegetable oils from Macauba fruit. Journal of Analytical and Applied Pyrolysis 2004;72:103–11.
[24] Alencar JW, Alves PB, Craveiro AA. Pyrolysis of tropical vegetable-oils. Journal of Agricultural and Food Chemistry 1983;31:1268–70.
[25] Li H, Yu P, Shen B. Biofuel potential production from cottonseed oil: a comparison of non-catalytic and catalytic pyrolysis on fixed-fluidized bed reactor. Fuel Processing Technology 2009;90:1087–92.
[26] Ngo TA, Kim J, Kim SK, Kim SS. Pyrolysis of soybean oil with H-ZSM5 and MCM41 catalysts in a fixed-bed reactor. Energy 2010;35:2723–8.
[27] Prado CMR, Antoniosi Filho NR. Production and characterization of the biofuels obtained by thermal cracking and thermal catalytic cracking of vegetable oils. Journal of Analytical and Applied Pyrolysis 2009;86: 338–347.
[28] Luo Y, Ahmed I, Kubátová A, Šťávová J, Aulich T, Sadrameli SM, Seames WS. The thermal cracking of soybean/canola oils and their methyl esters. Fuel Processing Technology 2010;91:613–7.
[29] Junming X, Jianchun J, Yunjuan S, Jie C. Production of hydrocarbon fuels from pyrolysis of soybean oils using a basic catalyst. Bioresource Technology 2010;101:9803–6.
[30] Idem RO, Katikaneni SPR, Bakhshi NN. Catalytic conversion of canola oil to fuels and chemicals: roles of catalyst acidity, basicity and shape selectivity on product distribution. Fuel Processing Technology 1997;51:101–25.
[31] Dandik L, Aksoy HA. Effect of catalyst on the pyrolysis of used oil carried out in a fractionating pyrolysis reactor. Renewable Energy 1999;16: 1007–1010.
[32] Twaiq FA, Zabidi NAM, Mohamed AR, Bhatia S. Catalytic conversion of palm oil over mesoporous aluminosilicate MCM-41 for the production of liquid hydrocarbon fuels. Fuel Processing Technology 2003;84:105–20.
[33] Onay O, Kockar OM. Pyrolysis of rapeseed in a free fall reactor for production of biooil. Fuel 2006;85:1921–8.
[34] Doll KM, Sharma BK, Suarez PAZ, Erhan SZ. Comparing biofuels obtained from pyrolysis, of soybean oil or soapstock, with traditional soybean biodiesel: density, kinematic viscosity, and surface tensions. Energy and Fuels 2008;22:2061–6.
[35] Wiggers VR, Meier HF, Wisniewski Jr. A, Chivanga Barros AA, Wolf Maciel MR. Biofuels from continuous fast pyrolysis of soybean oil: a pilot plant study. Bioresource Technology 2009;100:6570–7.
[36] Songthanapitak N, Trusabunjong W, Bumrungchukiet O, Popuang S. Pyrolysis of palm oil by thermal cracking. 〈http://ebookbrowse.com/gdoc.php?id=85449276&url=ca6a77edcfab06ff2c38d8ea25a650f0〉.
[37] Ong YK, Bhatia S. The current status and perspectives of biofuel production via catalytic cracking of edible and non-edible oils. Energy 2010;35:111–9.
[38] Weisz PB, Haag WO, Rodewald PG. Catalytic production of high-grade fuel (gasoline) from biomass compounds by shape-selective catalysts. Science 1979;206:57–8.
[39] Dos Anjos JRS, De Araujo Gonzalez W, Yiu Lau R. Lam, Catalytic decomposition of vegetable oil. Applied Catalysis 1983;5:299–308.
[40] Dandik L, Aksoy HA, Erdem-Senatalar A. Catalytic conversion of used oil to hydrocarbon fuels in a fractionating pyrolysis reactor. Energy and Fuels 1998;12:1148–52.
[41] Siregar TB, Amin NAS. Catalytic cracking of palm oil to gasoline over pretreated Cu-ZSM-5. Jurnal Teknologi 2006;44:69–82.
[42] Buzetzki E, Švaňová K, Cvengrošová Z, Mikulec J, Kaszonyi A, Cvengroš J. Liquid condensates from oil/fat cracking as components of blended diesel fuels. In: Proceedings of the 44th international petroleum conference. Bratislava, Slovak Republic; 2009. p. 1–10.
[43] Dandik L, Aksoy HA. Pyrolysis of used sunflower oil in the presence of sodium carbonate by using fractionating pyrolysis reactor. Fuel Processing Technology 1998;57:81–92.
[44] Junming X, Jianchun J, Yanju L, Jie C. Liquid hydrocarbon fuels obtained by the pyrolysis of soybean oils. Bioresource Technology 2009;100: 4867–70.
[45] Bezergianni S, Voutetakis S, Kalogianni A. Catalytic hydrocracking of fresh and used cooking oil. Industrial & Engineering Chemistry Research 2009;48:8402–6.
[46] Tamunaidu P. Biofuel production from crude palm oil and used palm oil in a transport riser catalytic reactor. Master thesis. Universiti Sains Malaysia, Malaysia; 2006.
[47] Corma A, Huber GW, Sauvanaud L, O'Connor P. Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. Journal of Catalysis 2007;247:307–27.
[48] Soares RR, Simonetti DA, Dumesic JA. Angewandte Chemie International Edition 2006;45:3982–5.
[49] Van Gerpen J, Shanks B, Pruszko R, Clements D, Knothe G. Biodiesel production technology. Subcontractor report. National Renewable Energy Laboratory NREL/SR-510-36244, cited by A. Karmakar et al. Bioresource Technology 2004;101(2010):7201–10.
[50] Billaud F, Guitard Y, Tran Minh AK, Zahraa O, Lozano P, Pioch D. Kinetic studies of catalytic cracking of octanoic acid. Journal of Molecular Catalysis A: Chemical 2003;192:281–8.
[51] Hites RA, Bieman K. On the mechanism of ketonic decarboxylation. Pyrolysis of calcium decanoate. Journal of the American Chemical Society 1972;94:5772–7.
[52] Vonghia E, Boocock DGB, Konar SK, Leung A. Pathways for the deoxygenation of triglycerides to aliphatic hydrocarbons over activated alumina. Energy and Fuels 1995;9:1090–6.
[53] Ooi YS, Zakaria R, Mohamed AR, Bhatia S. Catalytic conversion of palm oil based fatty acid mixture to liquid fuel. Biomass and Bioenergy 2004;27: 477–84.
[54] Kubickova I, Snare M, Eranen K, Maki-Arvela P, Murzin DY. Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. Catalysis Today 2005;106:197–200.
[55] Lestari S, Maki-Arvela P, Bernas H, Simakova O, Sjoholm R, Beltramini J, Lu GQM, Myllyoja J, Simakova I, Murzin DY. Catalytic deoxygenation of stearic acid in a continuous reactor over a mesoporous carbon-supported Pd catalyst. Energy and Fuels 2009;23:3842–5.
[56] Simakova I, Simakova O, Maki-Arvela P, Simakov A, Estrada M, Murzin DY. Deoxygenation of stearic acid over supported Pd catalysts: effect of metal dispersion. Applied Catalysis A—General 2009;355:100–8.
[57] Hsu HL, Osburn JO, Grove CS. Pyrolysis of the calcium salts of fatty acids. Industrial and Engineering Chemistry 1950;42:2141–5.
[58] Fortes ICP, Baugh PJ. Study of calcium soap pyrolysates derived from Macauba fruit (*Acrocomia sclerocarpa* M.)—derivatization and analysis by GC/MS and CI-Ms. Journal of Analytical and Applied Pyrolysis 1994;29:153–67.
[59] Lappi H, Alén R. Production of vegetable oil-based biofuels—thermochemical behavior of fatty acid sodium salts during pyrolysis. Journal of Analytical and Applied Pyrolysis 2009;86:274–80.
[60] Crossley A, Heyes TD, Hudson BJF. Effect of heat on pure triglycerides. Journal of the American Oil Chemists Society. 1962;39:9–14.
[61] Tian H, Li CY, Yang CH, Shan HH. Conversion of animal fat over various catalysts. Chinese Journal of Catalysis. 2008;29:69–74.

[62] Slinn M, Kendall K, Mellon K, Andrews J. Steam reforming of biodiesel byproduct to make renewable hydrogen. Bioresource Technology 2008;99:5851–8.
[63] Binlin D, Dupont V, Williams PT, Chen H, Ding Y. Thermogravimetric kinetics of crude glycerol. Bioresource Technology 2009;100:2613–20.
[64] Zander HJ, Wellhofer A, Behrens A, Korn W. Process and device for gasification of crude glycerol. Patent; 2009.
[65] Stein YS, Antal MJ, Jones M. A study of gas phase pyrolysis of glycerol. Journal of Analytical and Applied Pyrolysis 1983;4:283–96.
[66] Huber GW, Corma A. Synergies between bio-and oil refineries for the production of fuels from biomass. Angewandte Chemie International Edition 2007;46:7184–201.
[67] Van de Velden M, Baeyens J, Brems A, Janssens B, Dewil R. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. Renewable Energy 2010;35:232–42.
[68] Shen DK, Gu S, Bridgwater AV. The thermal performance of the polysaccarides entracte from hardwood: cellulose and hemicelluloses. Carbohydrate Polymers 2010;82:39–45.
[69] Lin YC, Cho J, Tompsett GA, Westmoreland PR, Huber GW. Kinetics and mechanism of cellulose pyrolysis. Journal of Physical Chemistry C 2009;113(2009):7–20107.
[70] Liao YF, Wang SR, Ma XQ. Study Of reaction mechanisms in cellulose pyrolysis, Preprint Papers—American Chemical Society. Division of Fuel Chemistry 2004;49:407–11.
[71] Kawamoto H, Saito S, Saka S. Inhibition of acid-catalyzed depolymerization of cellulose with boric acid in non-aqueous acidic media. Carbohydrate Research 2008;343:249–55.
[72] Dobele G, Rossinskaja G, Dizhbite T, Telysheva G, Meier D, Faix O. Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis. Journal of Analytical and Applied Pyrolysis 2005;74:401–5.
[73] Cozzani V, Petarca L, Tognotti L. Devolatilization and pyrolysis of refuse derived fuels: characterization and kinetic modelling by thermogravimetric and calorimetric approach. Fuel 1995;74:903–12.
[74] Putun AE. Biomass to bio-oil via fast pyrolysis of cotton straw and stalk. Energy Sources 2002;24:275–85.
[75] Zheng J, Yi W, Wang N. Bio-oil production from cotton stalk. Energy Conversion and Management 2008;49:1724–30.
[76] Peng Y, Wu S. The structural and thermal characteristics of wheat straw hemicellulose. Journal of Analytical and Applied Pyrolysis 2010;88:134–9.
[77] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for biooil: a critical review. Energy and Fuels 2006;20:848–89.
[78] Paris O, Zollfrank C, Zickler GA. Decomposition and carbonization of wood biopolymers—a microstructural study of softwood pyrolysis. Carbon 2005;43:53–66.
[79] Shen DK, Gua S, Luo KH, Wang SR, Fang MX. The pyrolytic degradation of wood-derived lignin from pulping process. Bioresource Technology 2010;101:6136–46.
[80] Mullen CA, Boateng AA. Characterization of water insoluble solids isolated from various biomass fast pyrolysis oils. Journal of Analytical and Applied Pyrolysis 2011;90:197–203.
[81] Ferdous D, Dalai AK, Bej SK, Thring RW, Bakhshi NN. Production of H_2 and medium Btu gas via pyrolysis of lignins in a fixed-bed reactor. Fuel Processing Technology 2001;70:9–26.
[82] Thring RW, Katikaneni SPR, Bakhshi NN. The production of gasoline range hydrocarbons from Alcell® lignin using HZSM-5 catalyst. Fuel Processing Technology 2000;62:17–30.
[83] Neves D, Thunman H, Matos A, Tarelho L, Gomez-Barea A. Characterization and prediction of biomass pyrolysis products. Progress in Energy and Combustion Science . 2011;37:611–30.
[84] Huang YF, Kuan WH, Chiueh PT, Lo SL. Pyrolysis of biomass by thermal analysis–mass spectrometry (TA–MS). Bioresource Technology 2011;102:3527–34.
[85] Keane MA. Catalytic transformation of waste polymers to fuel oil. ChemSusChem 2009;2:207–14.
[86] Shah J, Rasul MJ, Mabood F, Jabeen F. Catalytic pyrolysis of LDPE leads to valuable resource recovery and reduction of waste problems. Energy Conversion and Management 2010;51 2791-2280.
[87] Kumar S, Panda AK, Singh RK. A review on tertiary recycling of high-density polyethylene to fuel. Conservation and Recycling 2011;55:893–910.
[88] Aguado J, Serrano DP, San G, Miguel JM, Escola JM. Rodriguez Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins. Journal of Analytical and Applied Pyrolysis 2007;78:153–61.
[89] J. Aguado, D.P. Serrano, J.H. Clark, Feedstock Recycling Of Plastic Wastes, The Royal Society of Chemistry, Series ed.., Cambridge, 1999.
[90] Onwudili JA, Insura N, Williams PT. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: effects of temperature and residence time. Journal of Analytical and Applied Pyrolysis 2009;86:293–303.
[91] Lee KH. Pyrolysis of municipal plastic wastes separated by difference of specific gravity. Journal of Analytical and Applied Pyrolysis 2007;79:362–7.
[92] Manos G, Garforth AA, Dwyer J. Catalytic degradation of high-density polyethylene over different zeolitic structures. Industrial & Engineering Chemistry Research 2000;39:1198–202.
[93] Bonilla A, Baudouin D, Pérez-Ramírez J. Desilication of ferrierite zeolite for porosity generation and improved effectiveness in polyethylene pyrolysis. Journal of Catalysis 2009;265:170–80.
[94] Uemichi Y, Takuma K, Ayame A. Chemical recycling of poly(ethylene) by catalytic degradation into aromatic hydrocarbons using H-Ga-Silicate. Chemical Communications 1998;40:1975–6.
[95] Takuma K, Uemichi Y, Sugioka M, Ayame A. Production of aromatic hydrocarbons by catalytic degradation of polyolefins over H-gallosilicate. Industrial & Engineering Chemistry Research 2001;40:1076–81.
[96] Nishino J, Itoh M, Ishinomori T, Kubota N, Uemichi Y. Development of a catalytic cracking process for converting waste plastics to petrochemicals. Journal of Material Cycles and Waste Management 2003;5:89–93.
[97] Nishino J, Itoh M, Fujiyoshi H, Ishinomori T, Kubota N. Development of a feedstock recycling process for converting waste plastics to petrochemicals. IHI Engineering Review 2004;37:64–70.
[98] Nishino J, Itoh M, Fujiyoshi H, Uemichi Y. Catalytic degradation of plastic waste into petrochemicals using Ga-ZSM-5. Fuel 2008;87:3681–6.
[99] Wong HW, Broadbelt LJ. Tertiary resource recovery from waste polymers via pyrolysis: neat and binary mixture reactions of polypropylene and polystyrene. Industrial & Engineering Chemistry Research 2001;40: 4716–23.
[100] Panda AK, Singh RK. Catalytic performances of kaoline and silica alumina in the thermal degradation of polypropylene. Journal of Fuel Chemistry and Technology 2011;39:198–202.
[101] Chauhan RS, Gopinath S, Razdan P, Delattre C, Nirmala GS, Natarajan R. Thermal decomposition of expanded polystyrene in a pebble bed reactor to get higher liquid fraction yield at low temperatures. Waste Management 2008;28:2140–5.
[102] Barlow A, Lehrle RS, Robb JC, Sunderland D. Polymethylmethacrylate degradation-kinetics and mechanisms in the temperature range 340–460 °C. Polymer 1967;8:537–45.
[103] Lopez G, Artetxe M, Amutio M, Elordi G, Aguado R, OlazarJ. M. Bilbao, Recycling poly-(methyl methacrylate) by pyrolysis in a conical spouted bed reactor. Chemical Engineering and Processing 2010;49:1089–94.
[104] Kaminsky W, Franck J. Monomer recovery by pyrolysis of poly(methyl methacrylate) (PMMA). Journal of Analytical and Applied Pyrolysis 1991;19:311–8.
[105] Kaminsky W, Eger C. Pyrolysis of filled PMMA for monomer recovery. Journal of Analytical and Applied Pyrolysis 2001;58–59:781–7.
[106] Grause G, Handa T, Kameda T, Mizoguchi T, Yoshioka T. Effect of temperature management on the hydrolytic degradation of PET in a calcium oxide filled tube reactor. Chemical Engineering Journal 2011;166: 523–8.
[107] Artetxe M, Lopez G, Amutio M, Elordi G, OlazarJ. M. Bilbao Operating conditions for the pyrolysis of poly-(ethylene terephthalate) in a conical spouted-bed reactor. Industrial & Engineering Chemistry Research 2010;49:2064–9.
[108] Yoshioka T, Grauseb G, Eger C, Kaminsky W, Okuwaki A. Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant. Polymer Degradation and Stability 2004;86:499–504.
[109] Martın-Gullon I, Esperanza M, Font R. Kinetic model for the pyrolysis and combustion of poly-(ethylene terephthalate) (PET). Journal of Analytical and Applied Pyrolysis 2001;58–59:635–50.
[110] Williams PT, Williams EA. Interaction of plastics in mixed-plastics pyrolysis. Energy and Fuels 1999;13:188–96.
[111] Masuda T, Miwa Y, Hashimoto K, Ikeda Y. Recovery of oil from waste poly(ethylene terephthalate) without producing any sublimate materials. Polymer Degradation and Stability 1998;61:217–24.
[112] Grause G, Handa T, Kameda T, Mizoguchi T, Yoshioka T. Effect of temperature management on the hydrolytic degradation of PET in a calcium oxide filled tube reactor. Chemical Engineering Journal 2011;166: 523–8.
[113] German K. Influence of the presence of poly(oxymethylene) on the pyrolysis oil from poly(vinyl chloride). Journal of Analytical and Applied Pyrolysis 2008;82:260–3.
[114] Ma S, Lu J, Gao J. Study of the low temperature pyrolysis of PVC. Energy and Fuels 2002;16:338–42.
[115] Zhu HM, Jiang XG, Yan JH, Chi Y, Cen KF. TG-FTIR analysis of PVC thermal degradation and HCl removal. Journal of Analytical and Applied Pyrolysis 2008;82:1–9.
[116] López A, de Marco I, Caballero BM, Laresgoiti MF, Adrados A. Dechlorination of fuels in pyrolysis of PVC containing plastic wastes. Fuel Processing Technology 2011;92:253–60.
[117] Ragazzi M, Ischia M, Dal Maschio R, Rada EC, Grigiante M, Baratieri M. Disposal of PVC by pyrolysis: characterization of the process and labscale reactor tests. In: Proceedings of the 3rd international symposium energy from biomass and waste, Venice; 2010 [available on the web].
[118] Sun Q, Shi X, Lin Y, Zhu H, Wang X, Cheng C, Liu J. Thermogravimetric-mass spectrometric study of the pyrolysis behavior of PVC. Journal of China University of Mining & Technology 2007;17:242–5.
[119] Czernik S, Elam CC, Evans RJ, Meglen RR, Moens L, Tatsumoto K. Catalytic pyrolysis of nylon-6 to recover caprolactam. Journal of Analytical and Applied Pyrolysis 1998;46:51–64.
[120] Lehrle RS, Parsons IW, Rollinson M. Thermal degradation mechanisms of Nylon 6 deduced from kinetic studies by pyrolysis-g.c. Polymer Degradation and Stability 2000;67:21–33.
[121] Bockhorn H, Donner S, Gernsbeck M, Hornung A, Hornung U. Pyrolysis of polyamide 6 under catalytic conditions and its application to reutilization of carpets. Journal of Analytical and Applied Pyrolysis 2001;58–59: 79–94.

[122] Herrera M, Matuschek G, Kettrup A. Thermal degradation studies of some aliphatic polyamides using hyphenated techniques (TG-MS, TG-FTIR). Journal of Thermal Analysis and Calorimetry 2000;59:385–94.
[123] Schaffer MA, Marchildon EK, McAuley KB, Cunningham MF. Thermal non oxidative degradation of Nylon 6,6. Journal of Macromolecular Science - Reviews in Macromolecular Chemistry & Physics 2000;C40: 233–272.
[124] Day M, Cooney JD, Touchette-Barrette C, Sheehan SE. Pyrolysis of mixed plastics used in the electronics industry. Journal of Analytical and Applied Pyrolysis 1999;52:199–224.
[125] Brebu M, Azhar Uddin M, Muto A, Sakata Y, Vasile C. The role of temperature program and catalytic system on the quality of acrylonitrile-butadiene-styrene degradation oil. Journal of Analytical and Applied Pyrolysis 2002;63:43–57.
[126] Zia KM, Bhatti HN, Bhatti IA. Methods for polyurethane and polyurethane composites, recycling and recovery: a review. Reactive and Functional Polymers 2007;67:675–92.
[127] Lattimer RP, Polce MJ, Wesdemiotis C. MALDI-MS analysis of pyrolysis products from a segmented polyurethane. Journal of Analytical and Applied Pyrolysis 1998;48:1–15.
[128] Lattimer RP, Williams RC. Low-temperature pyrolysis products from a polyether-based urethane. Journal of Analytical and Applied Pyrolysis 2002;63:85–104.
[129] Zhang Y, Xia Z, Huang H, Chen H. Thermal degradation of polyurethane based on IPD. Journal of Analytical and Applied Pyrolysis 2009;84:89–94.
[130] Zhang Y, Xia Z, Huang H, Chen H. A degradation study of waterborne polyurethane based on TDI. Polymer Testing 2009;28:264–326.
[131] Rogaume Y, Jabouille F, Auzanneau M, Goudeau JC. Proceedings of the fifth international conference on technologies and combustion for a clean environment, vol. 1. Lisbon, Portugal; 1999. p. 345–51.
[132] Bilbao R, Mastral JF, Ceamanos J, Aldea ME. Kinetics of the thermal decomposition of polyurethane foams in nitrogen and air atmosphere. Journal of Analytical and Applied Pyrolysis 1996;37:69–82.
[133] Takamoto DY, Petrich MA. Effect of heterogeneous secondary pyrolysis reactions on the thermal decomposition of polyurethane scrap. Industrial & Engineering Chemistry Research 1994;33:3004–9.
[134] Font R, Fullana A, Caballero JA, Candela J, Garcıa A. Pyrolysis study of polyurethane. Journal of Analytical and Applied Pyrolysis 2001;58–59: 63–77.
[135] Szabo E, Olah M, Ronkay F, Miskolczi N, Blazso M. Characterization of the liquid product recovered through pyrolysis of PMMA–ABS waste. Journal of Analytical and Applied Pyrolysis 2011;92:19–24.
[136] Miskolczi N, Bartha L, Angyal A. Pyrolysis of polyvinyl chloride (PVC)-containing mixed plastic wastes for recovery of hydrocarbons. Energy and Fuels 2009;23:2743–9.
[137] Laresgoiti MF, Carballero BM, de Marco I, Torres A, Cabroero MA, Chomon MJ. Characterization of the liquid products obtained in tyre pyrolysis. Journal of Analytical and Applied Pyrolysis 2004;71:917–34.
[138] Barbooti MM, Mohamed TJ, Hussain AA, Abas FO. Optimization of pyrolysis conditions of scrap tires under inert gas atmosphere. Journal of Analytical and Applied Pyrolysis 2004;72:165–70.
[139] Qu W, Zhou Q, Wang YZ, Zhang J, Lan WW, Wu YH, Yang JW, Wang DZ. Pyrolysis of waste tire on ZSM-5 zeolite with enhanced catalytic activities. Polymer Degradation and Stability 2006;91:2389–95.
[140] Williams PT, Brindle AJ. Catalytic pyrolysis of tyres: influence of catalyst temperature. Fuel 2002;81:2425–34.
[141] Williams PT, Brindle AJ. Fluidised bed catalytic pyrolysis of scrap tyres. Waste Management and Research 2002;20:546–55.
[142] Williams PT, Brindle AJ. Aromatic chemicals from the catalytic pyrolysis of scrap tyres. Journal of Analytical and Applied Pyrolysis 2003;67: 143–64.
[143] Zabaniotou AA, Stavropoulos G. Pyrolysis of used automobile tires and residual char utilization. Journal of Analytical and Applied Pyrolysis 2003;70:711–22.
[144] Pakdel H, Pantea DM, Roy C. Production of dl-limonene by vacuum pyrolysis of used tires. Journal of Analytical and Applied Pyrolysis 2001;57: 91–107.
[145] Yanik J, Uddin MA, Sakata Y. The effect of red mud on the liquefaction of waste plastics in heavy vacuum gas oil. Energy and Fuels 2001;15:163–9.
[146] Lin HT, Huang MS, Luo JW, Lin LH, Lee CM, Ou KL. Hydrocarbon fuels produced by catalytic pyrolysis of hospital plastic wastes in a fluidizing cracking process. Fuel Processing Technology 2010;91:1355–63.
[147] Huang WC, Huang MS, Huang CF, Chen CC, Ou KL. Thermochemical conversion of polymer wastes into hydrocarbon fuels over various fluidizing cracking catalysts. Fuel 2010;89:2305–16.
[148] Harder MK, Forton OT. A critical review of developments in the pyrolysis of automotive shredder residue. Journal of Analytical and Applied Pyrolysis 2007;79:387–94.
[149] Vermeulen I, Van Caneghem J, Block C, Baeyens J, Vandecasteele C. Automotive shredder Residue (ASR): reviewing its production from end-of-life vehicles (ELVs) and its recycling, energy or chemicals' valorisation. Journal of Hazardous Materials 2011;190:8–27.
[150] Donaj P, Blasiak W, Yang W, Forsgren C. Conversion of microwave pyrolysed ASR's char using high temperature agents. Journal of Hazardous Materials 2011;185:472–81.
[151] Zolezzi M, Nicolella C, Ferrara S, Lacobucci C, Rovatti M. Conventional and fast pyrolysis of automobile shredder residue (ASR). Waste Management. 2004;24:691–9.
[152] de Marco I, Caballero B, Cabrero MA, Laresgoiti MF, Torres A, Chomon MJ. Recycling of automobile shredder residues by means of pyrolysis. Journal of Analytical and Applied Pyrolysis 2007;79:403–8.
[153] Noureddine M. Recycling of auto shredder residue. Journal of Hazardous Materials 2007;A139:481–91.
[154] Buah WK, Cunliffe AM, Williams PT. Characterization of products from the pyrolysis of municipal solid waste. Institution of Chemical Engineers 2007;85(B5):450–7.
[155] Roy C, de Cumbia B, Pakdel H, Couture G, Labrecque B. Treatment of biomass and municipal solid waste by vacuum pyrolysis. In: Bridgewater, Kuester, editors. Research in Thermochemical Biomass Conversion. London: Elsevier Applied Science; 1988.
[156] Rampling TW, Hickey TJ. The laboratory characterization of refuse derived fuel, Warren Spring Laboratory, report no LR643. London: Department of Trade and Industry, HM Government, HMSO; 1988.
[157] Lin KS, Wang HP, Liu SH, Chang NB, Huang YJ, Wang HC. Pyrolysis kinetics of refuse-derived fuel. Fuel Processing Technology 1999;60:103–10.
[158] Paradela F, Pinto F, Ramos AM, Gulyurtlu I, Cabrita I. Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes. Journal of Analytical and Applied Pyrolysis 2009;85:392–8.
[159] Phan AN, Ryu C, Sharifi VN, Swithenbank J. Characterisation of slow pyrolysis products from segregated wastes for energy production. Journal of Analytical and Applied Pyrolysis 2008;81:65–71.
[160] Sørum L, Grønli MG, Hustad GE. Pyrolysis characteristics and kinetics of municipal solid wastes. Fuel 2001;80:1217–27.
[161] Shen L, Zhang D. Low-temperature pyrolysis of sewage sludge and putrescible garbage for fuel oil production. Fuel 2005;84:809–15.
[162] Park HJ, Heo HS, Park Y, Yim J, Jeon J, Park J, Ryu C, Kim S. Clean bio-oil production from fast pyrolysis of sewage sludge: effects of reaction conditions and metal oxide catalysts. Bioresource Technology 2010;101:S83.
[163] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass: review article. Fuel 2010;89: 913–933.
[164] Buklushev DA, Ross JRH. Catalysis for the conversion of biomass to fuels via pyrolysis. Catalysis Today 2011;171:1–13.
[165] Katikaneni SPR, Adjaye JD, Bakhshi NN. Catalytic conversion of canola oil to fuels and chemicals over various cracking catalysts. Canadian Journal of Chemical Engineering 1995;73:484–97.
[166] Twaiq FA, Mohamed AR, Bhatia S. Liquid hydrocarbon fuels from palm oil by catalytic cracking over mesoporous aluminosilicate catalysts with various Si/Al ratio. Microporous and Mesoporous Materials 2003;64:95–107.
[167] Ooi YS, Zacharia R, Mohamed AR, Bhatia S. Hydrothermal stability and catalytic activity of mesoporous aluminum-containing SBA-15. Catalysis Communications. 2004;5:441–5.
[168] Ooi YS, Bhatia S. Aluminum-containing SBA-15 as cracking catalyst for the production of biofuel from waste used palm oil. Microporous and Mesoporous Materials 2007;102:310–7.
[169] Twaiq FA, Zabidi NAM, Bhatia S. Catalytic conversion of palm oil to hydrocarbons: performance of various zeolite catalysts. Industrial & Engineering Chemistry Research 1999;38:3230–8.
[170] Twaiq FA, Mohamed AR, Bhatia S. Performances of composite catalysts in palm oil cracking for the production of liquid fuels and chemicals. Catalytic conversion of palm oil over mesoporous aluminosilicate MCM-41 for the production of liquid hydrocarbon fuels. Fuel Processing Technology 2004;85:1283–300.
[171] Tamunaidu P, Bhatia S. Catalytic cracking of palm oil for the production of biofuels: optimization studies. Bioresource Technology 2007;98:3593–601.
[172] Chew TL, Bhatia S. Effect of catalyst additives on the production of biofuels from palm oil cracking in a transport riser reactor. Bioresource Technology 2009;100:2540–5.
[173] Katikaneni SPR, Adjaye JD, Bakhshi NN. Studies on the catalytic conversion of canola oil to hydrocarbons: influence of hybrid catalysts and steam. Energy and Fuels 1995;9:599–609.
[174] Melero JA, Clavero MM, Calleja G, Garcia A, Miravalles R, Galindo T. Production of biofuels via the catalytic cracking of mixtures of crude vegetable oils and nonedible animal fats with vacuum gas oil. Energy and Fuels 2010;24:707–17.
[175] Tian H, Li C, Yang C, Shan H. Alternative processing technology for converting vegetable oils and animal fats to clean fuels and light olefins. Chinese Journal of Chemical Engineering 2008;16:394–400.
[176] Pearl GG. Animal fats and recycled coking oils, alternatives as burner fuels. 〈http://fatforfuel.us/images/GaryPearl.pdf〉; 2001.
[177] Adams TT. A demonstration of fat and grease as an industrial boiler fuel. Project report of University of Georgia, USA. 〈http://www.biorefinery.uga.edu/docs/biofuel_oil_report.pdf〉; 2002.
[178] Masia AAT, Buhre BJP, Gupta RP, Wall TF. Characterising ash of biomass and waste. Fuel Processing Technology 2007;88:1071–81.
[179] Chang ACC, Chang HF, Lin FJ, Lin KH, Chen CH. Biomass gasification for hydrogen production. International Journal of Hydrogen Energy, in press.
[180] Tihay V, Boulnois C, Gillard P. Influence of oxygen concentration on the kinetics of cellulose wadding degradation. Thermochimica Acta, in press.

[181] Skreiberg A, Skreiberg Ø, Sandquist J, Sørum L. TGA and macro-TGA characterization of biomass fuels and fuel mixtures. Fuel 2011;90: 2182–2197.
[182] Zhu HM, Yan JH, Jiang XG, Lai YE, Cen KF. Study on pyrolysis of typical medical waste materials by using TG-FTIR analysis. Journal of Hazardous Materials 2008;153:670–6.
[183] Lin YH, Tseng CC, Wei TT, Hsu CT. Recycling of dual hazardous wastes in a catalytic fluidizing process. Catalysis Today 2011;174:37–45.
[184] Bryers RW. Fireside slagging, fouling and high-temperature corrosion of heat transfer surface due to impurities in steam raising fuels. Progress in Energy and Combustion Science 1996;22:29–120.
[185] Miles TR, Miles JTR, Baxter LL, Bryers RW, Jenkins BM, Oden LL. Alkali deposits found in biomass power plants. A preliminary investigation of their extent and nature. Report of the National Renewable Energy Laboratory (NREL/TZ-2- 11226-1; TP-433-8142). Golden, CO, USA; 1995.
[186] Moilanen A. Thermogravimetric characterisations of biomass and waste for gasification processes. VTT Technical Research Centre of Finland. Publications no. 607; 2006. p. 103.
[187] Wei X, Schnell U, Hein KRG. Behaviour of gaseous chlorine and alkali metals during biomass thermal utilisation. Fuel 2005;84:841–8.
[188] Thy P, Jenkins BM, Grundvig S, Shiraki R, Lesher CE. High temperature elemental losses and mineralogical changes in common biomass ashes. Fuel 2006;85:783–95.
[189] Nutalapati D, Gupta R, Moghtaderi B, Wall TF. Assessing slagging and fouling during biomass combustion: a thermodynamic approach allowing for alkali/ash reactions. Fuel Processing Technology 2007;88:1044–52.
[190] Werther J, Saenger M, Hartge EU, Ogada T, Siagi Z. Combustion of agricultural residues. Progress in Energy and Combustion Science 2000;26:1–27.
[191] Lapuerta M, Hernandez JJ, Pazo A, Lopez J. Gasification and co-gasification of biomass wastes: effect of the biomass origin and the gasifier operating conditions. Fuel Processing Technology 2008;89:828–37.
[192] Demirbas A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. Progress in Energy and Combustion Science 2005;31:171–92.
[193] Madhiyanon T, Sathitruangsak P, Soponronnarit S. Co-combustion of rice husk with coal in a cyclonic fluidized-bed combustor (W-FBC). Fuel 2009;88: 132–8.
[194] Tite MS, Shortland A, Maniatis Y, Kavoussanaki D, Harris SA. The composition of the soda-rich and mixed alkali plant ashes used in the production of glass. Journal of Archaeological Science 2006;33:1284–92.
[195] Ross AB, Jones JM, Kubacki ML, Bridgeman T. Classification of macroalgae as fuel and its thermochemical behaviour. Bioresource Technology 2008;99: 6494–504.
[196] U.S. Army Corps of Engineers. Technical instructions, waste incinerations, 1998, TI 814–821.
[197] Oh SC, Kwon WT, Kim SR. Dehydrochlorination characteristics of waste PVC wires by thermal decomposition. J. Ind. Eng. Chem. 2009;15:438–41.
[198] Mirabile D, Pistelli MI, Marchesini M, Falciani R. Thermal valorisation of automobile shredder residue injection in blast furnace. Waste Management. 2002;22:841–51.
[199] Rausa R, Pollesel P. Pyrolysis of automotive shredder residue (ASR); influence of temperature on the distribution of products. Journal of Analytical and Applied Pyrolysis 1997;40–41:383–401.
[200] Fuentes MJ, Font R, Gómez-Rico MF, Martín-Gullón I. Pyrolysis and combustion of waste lubricant oil from diesel cars: Decomposition and pollutants. Journal of Analytical and Applied Pyrolysis 2007;79:215–26.
[201] Pettersson A, Zevenhoven M, Steenari BM, Amand LE. Application of chemical fractionation methods for characterisation of biofuels, waste derived fuels and CFB co-combustion fly ashes. Fuel 2008;87:3183–93.